JOURNAL OF

THE INSTITUTE OF PETROLEUM

FOUNDED 1913 + INCORPORATED 1914

Vol. 38 MAY 1952 No. 341

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Published by the Institute of Petroleum
26 Portland Place, London, W.1
Telephone No.: LANgham 2250
Telegraphic Address: Instpetech, Westdo, London
Printed in Great Britain by Richard Clay and Company, Ltd., Bungay, Suffolk

Price 10s.0d. Annual Subscription £4 14s. 6d. (Post Free)

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THE INSTITUTE OF PETROLEUM

An Ordinary General Meeting of the Institute of Petroleum was held at 26 Portland Place, London, W.1, on Wednesday, December 12, 1951, the President, Mr C. A. P. Southwell, M.C., in the Chair.

The President, opening the meeting and introducing the authors, said: I take this opportunity to say how glad I am to be back here after two months in the desert and to be able to join in the proceedings.

The authors of the paper we are to hear and discuss this evening are all members of the team at Birmingham University, headed by Professor Garner and Professor Morton. The work which has emanated from Birmingham in the past is sufficient guarantee that the account we are to hear this evening of further research work done in the Chemical Engineering Department there can be relied upon as being both accurate and informative.

In addition to Professor Garner and Professor Morton, their co-authors are Dr E. P. Wright, Mr W. D. Reid, Dr W. E. Malpas, and Dr A. H. Nissan, who, in the early stages, carried out some of the work which is contained in Part I of the paper.

I will ask Professor Garner if he will say a word or two about the work described, before we come to the paper proper.

Professor Garner, O.B.E. (Past-President): I wish to introduce Dr Wright, who will present the first part of the paper, the large number of names at the head of which is an indication of the fact that the work described has been going on for a long time.

The first part deals with a comparison between diesel additives in the liquid and vapour states, and that led us to consider the necessity of finding out what was taking place inside the diesel engine during pre-flame combustion, and to the development of the sampling valve.

The second part deals with the analysis of the various products formed in the pre-flame reactions. The second part should be considered as the preliminary work on this subject; since the paper was prepared further work has been done which has confirmed the conclusions reached.

Dr Wright then presented the following paper:

PRE-FLAME REACTIONS IN DIESEL ENGINES. PART I

By F. H. Garner, O.B.E. (*Past-President*), Frank Morton (*Vice-President*), A. H. Nissan (*Fellow*), and E. P. Wright (*Assoc. Fellow*)

It is well known that certain compounds, notably alkyl thionitrites, nitrites, nitrates, peroxides, and nitro-compounds improve the cetane number of diesel fuels when added to the fuel. Bogen and Wilson [1] have summarized the literature on this subject and have listed in order of effectiveness the

additives tested up to that time. In most cases, however, the additive was used dissolved in the fuel. Since the ignition of a diesel fuel spray appears to occur within a relatively limited zone and is followed by very rapid combustion, the additive present in the larger droplets is in all probability burnt in the combustion stage, and thus serves no useful purpose in promoting ignition. It might therefore be expected that addition of the additive to the air stream would result in a more effective utilization of these compounds.

Some experiments have been reported on the effect of various compounds when added to the intake air of a diesel engine. Gases such as methane,[2] ozone,[3] oxygen,[4] hydrogen,[4] and chlorine [5] have been studied. Porter [6] has reported a considerable improvement in the case of cold starting of diesel engines when chlorine, hydrogen sulphide, amyl nitrate, ethyl disulphide, trichloro-nitromethane, etc., were added to the intake air. Diethyl ether vaporized and drawn in with intake air was used as a cold-starting aid for automotive diesel engines during 1939–45,[7] and in Germany the injection of various alkyl ethers for the same purpose has been investigated.[8]

Although the effectiveness of additives in the air-intake stream as cold-starting aids is recognized, there is little data on the relative merits of such compounds and no quantitative data on the effect upon the cetane number of a given fuel of varying concentrations of the additive. It seemed desirable therefore to study the effect upon the cetane number of a number of typical diesel fuels of various additives when added to the fuel and when added with the intake air.

For this purpose six gas oils were chosen to give a range of chemical composition from paraffinic through paraffin–aromatic to naphthenic-type oils in order to establish the contribution made by the fuel used to the effectiveness of the additive. Tests were made with several gases and a large number of organic compounds. The tests were first carried out using a CFR F5 diesel fuel test engine.[9] Since the CFR diesel engine has a precombustion chamber of unusual design a second series of tests were performed using a Crossley type BVD-1 single-cylinder engine, which has a Ricardo " Comet " type precombustion chamber.

Apparatus

Ratings of the fuels to determine their cetane numbers were carried out on the CFR diesel fuel testing engine according to ASTM D.613–42T.[9] For the confirmatory tests on the Crossley engine a type BVD-1 engine was used, and ratings were carried out according to IP 41/48 (T) using the throttling procedure.[10]

In order to obtain consistent and reliable results it was important that the added gases or vaporized additives were thoroughly mixed with the air before entering the engine intake port. A large chamber with three internal baffles was therefore fitted to the air-intake pipe of the engine. This chamber was designed so that air drawn into it through a suitable venturi giving turbulent-flow conditions had the minimum of pulsation. The added gas or additive vapour was discharged from a small jet into the throat of the venturi, thus ensuring thorough mixing. A copper-gauze

cylinder was fitted inside this mixing chamber at its exit port to act as a flame arrestor.

Gases were obtained from high-pressure cylinders or suitable generators and passed through a flowmeter to the mixing jet at the venturi in the mixing chamber on the engine. When added gas was toxic, care was taken to ensure that the gas addition was carried out only while the engine was running, thus avoiding any danger of the gas escaping into the engine-room atmosphere.

The apparatus used for the addition of additives in the vapour phase to the intake air is outlined in Fig 1. Air from a high-pressure cylinder was dried and passed through two flowmeters into heating coils in a thermostatically controlled hot-water bath. One stream (the vaporizing air) then entered the vaporizer where it bubbled through the additive, and thus became saturated with its vapour. Leaving by the side arm, it passed

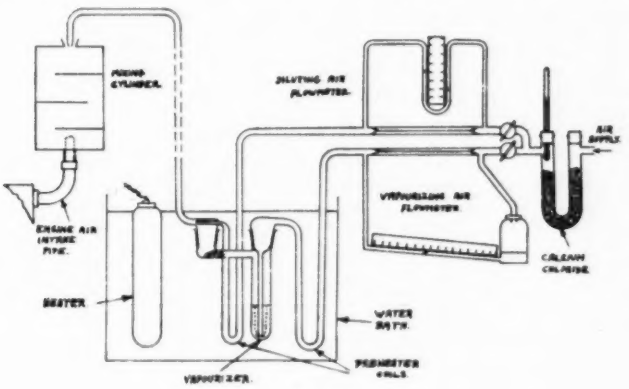

FIG 1

VAPOUR ADDITION APPARATUS FOR CFR ENGINE

through a glass-wool plug to collect any entrained droplets before leaving the vaporizer. The diluting air, having passed through its own preheating coil, then entered the vaporizer-outlet pipe through a small jet, where it mixed with the vapour-saturated vaporizing air. This brought the vapour/air concentration below that for saturation at room temperature, thus preventing deposition of the additive in the pipe which conveyed the vapour/air mixture to the mixing jet and venturi of the mixing chamber used for the addition of gases. By maintaining a constant rate of flow of air through the additive in the vaporizer over a measured period of time, the rate of addition of additive, which was assumed constant, was obtained.

For the confirmatory tests on the Crossley engine the vapour-saturated air was led directly to the short length of pipe leading to the throttle on the surge chamber. With this engine, constant control of the air supply to the vaporizing apparatus was required to compensate for variations in the air-suction pressure at the point of entry to the engine surge chamber arising from the manipulation of the throttle.

In order to avoid gas or additive vapour contamination of the air while

rating, a calibration curve for the engine was obtained with several blends of reference fuels. The gas or vapour-addition apparatus was then started up, and after an interval of 10 minutes the compression ratios for the standard 13° delay period (for the CFR engine) and the intake-suction pressures for misfire (for the Crossley engine) were determined for the various fuels plus the gas or vapour addition. A period of about 20 minutes then

TABLE I

Test fuel designation :	D.3	D.4	D.5	D.6	D.10	D.11
Sp. gr. at 60° F . .	0·846	0·839	0·845	0·890	0·842	0·856
Viscosity, Redwood I, at 100° F, sec .	35·6	34·1	33·5	35	36	34
Aniline point, ° C .	72·3	61·3	65·2	45·5	75·0	63·0
Pour point, ° F . .	10	5	Below 10	Below −40	15	−18° C
Flash point (closed), ° F	180	178	160	184	214	173
Cetane number . .	48·0	53·5	45·0	31·0	52·0	42·0
Conradson carbon on 10% bottoms, % .	0·20	0·35	0·10	0·34	0·11	0·03
Sulphur, % wt . .	—	—	—	—	0·71	0·56
Distillation :						
I.B.P., ° C . .	203	188	184	210	232	176
10% at . . .	235	215·5	214	230	258	—
20% at . . .	249	231	228	243	265·5	—
30% at . . .	261	248	239	249	272·5	—
40% at . . .	271·5	264	252	256	278·5	—
50% at . . .	283	281·5	264	264	284	—
60% at . . .	295	297·5	276	273	290·5	62% at 275
70% at . . .	308·5	313	289	284	298·5	77% at 300
80% at . . .	321·5	330	303	300	308·5	—
90% at . . .	337	349	322	323	323·5	91% at 350
F.B.P. . . .	361	362	362	367	365·5	—
Chemical composition .	Paraffinic	Paraffinic + olefins	Paraffin aromatic	Naphthenic	Paraffinic	Paraffin aromatic

elapsed to allow for the clearance of the vapour from the mixing cylinder, during which time the vaporizer was removed from the hot-water bath, dried, and weighed. A new calibration curve was then plotted and a further set of readings taken for the fuels with a different vaporizing air rate, and so on. Allowance was made in calculating the results for any shift in the calibration curve during this time.

FUELS

Inspection data on the six fuels are given in Table I. They were chosen to give a wide range of cetane number and chemical composition. D.3 is a gas oil from Eakring crude, D.4 is a shale oil, D.10 is a Middle East gas oil, D.5 and D.11 are Venezuelan gas oils, and D.6 is a highly naphthenic gas oil.

RESULTS

Addition to Fuel CFR Engine

Table II gives the experimental data on sixteen additives when added to various fuel oils and tested in the CFR engine. Although the accepted

reproducibility of results obtained on the CFR diesel engine is of the order of about 2 cetane numbers, the results given in Table II are probably more accurate than this figure. Each run with any one additive was carried out on the same day, and the results obtained can thus be taken to show the relative effect of varying quantities of additive in a fuel. In addition to the

TABLE II

Additive	% by vol	Fuels					
		D.3	D.4	D.5	D.6	D.10	D.11
Freon % wt	0	48·0	53·0	45·0	31·5	52·0	42·0
	2·87	52·5	54·0	48·0	33·5	54·5	44·0
Fluorobenzene	0	—	—	45·0	—	52·0	—
	0·5	—	—	52·5	—	60·0	—
	1·0	—	—	52·0	—	60·5	—
	2·0	—	—	49·5	—	57·0	—
Nitrobenzene	0	48·0	53·0	45·0	31·0	52·0	42·0
	1·0	56·0	59·0	54·0	34·5	62·0	51·0
	2·0	56·0	59·0	51·5	35·5	60·0	48·5
*iso*Amyl thio-nitrite	0	—	—	44·5	31·5	—	—
	1·0	—	—	59·0	40·5	—	—
	2·0	—	—	71·5	44·0	—	—
	3·0	—	—	77·5	—	—	—
tert-Butyl hydro-peroxide	0	48·0	—	45·0	31·0	52·0	—
	1·5	—	—	59·0	45·5	66·0	—
	2·0	—	—	63·0	—	—	—
	3·0	72·0	—	78·0	49·0	75·5	—
Benzene	0	51·5	—	—	32·5	58·5	44·0
	0·2	53·5	—	—	33·5	59·5	46·0
	0·6	54·5	—	—	33·5	61·0	46·5
	1·0	50·5	—	—	32·0	61·5	46·0
	2·0	50·5	—	—	31·0	59·0	44·0
1-Nitropropane	0·0	48·0	53·5	45·5	31·5	52·0	42·0
	1·0	50·0	—	—	32·0	54·5	43·0
	2·0	51·0	57·0	47·0	33·5	58·0	43·5
	4·0	—	—	—	34·5	—	—
	5·0	52·0	59·0	48·5	32·5	66·0	45·0
2-Nitropropane	0·0	47·5	54·0	—	32·0	52·0	—
	1·0	50·0	56·0	—	32·5	54·0	—
	2·0	50·0	58·0	—	33·0	56·5	—
	5·0	51·0	62·5	—	35·0	64·5	—
Diethylether	0·0	48·0	53·0	45·0	31·5	52·0	42·0
	1·5	51·5	54·0	48·0	32·5	56·0	47·0
	3·0	52·5	54·0	49·0	32·0	58·0	46·0
Carbon disulphide	0·0	48·0	53·0	45·0	31·5	52·0	42·0
	1·5	54·5	57·5	49·0	31·0	58·0	48·0
	3·0	54·0	54·5	48·5	29·5	57·0	48·5
Chloroform	0·0	48·0	53·0	45·0	31·5	52·0	42·0
	1·5	52·5	55·0	51·0	32·0	56·0	47·0
	3·0	54·5	57·0	50·5	31·5	56·5	46·5

additives listed in Table II many other compounds were investigated. For various reasons, *e.g.*, low solubility, instability, corrosive action, etc., these compounds have little theoretical or commercial significance, and have therefore been omitted from Table II.

From Table II it will be seen that *tert*-butyl hydroperoxide was the most effective additive tested, being slightly more effective than *iso*amylthionitrite. The effect of diethyl ether on cetane number is surprisingly small. Several additives, such as benzene, fluorobenzene, nitrobenzene, and several

TABLE III

Gas	% Gas to fuel (by wt)	Fuel					
		D.3	D.4	D.5	D.6	D.10	D.11
Oxygen	0	51·0	53·5	46·0	32·0	—	45·0
	0·57	51·5	54·0	45·0	32·5	—	44·0
	1·24	52·0	55·0	48·0	33·5	—	45·0
Nitrogen	0	51·0	53·5	46·0	32·0	56·0	45·0
	0·61	51·5	54·0	46·0	34·5	56·6	44·5
	1·33	50·5	55·0	46·0	35·0	55·0	44·0
Ammonia	0	51·0	53·5	46·0	32·0	—	45·0
	0·63	53·0	54·0	48·0	33·5	—	45·5
	1·28	52·0	56·0	49·0	35·0	—	45·0
Chlorine	0	51·0	53·5	46·0	32·0	56·0	45·0
	1·10	53·0	56·0	49·5	37·0	56·5	47·0
	2·31	53·0	52·5	49·0	35·0	57·5	48·5
Sulphur dioxide	0	51·0	53·5	46·0	32·0	—	45·0
	1·59	53·0	53·5	50·5	33·0	—	48·0
Hydrogen sulphide	0	51·0	53·5	46·0	32·0	56·0	45·0
	0·61	53·5	54·5	50·5	31·5	58·5	46·5
	1·42	53·0	54·0	48·5	34·0	58·5	48·0
Nitrous oxide	0	—	—	46·0	—	—	—
	0·81	—	—	44·5	—	—	—
	1·90	—	—	45·5	—	—	—
Methyl bromide	0	51·0	53·5	46·0	32·0	56·0	45·0
	0·12	54·5	53·5	45·0	32·5	54·5	44·0
	0·39	51·5	53·5	47·5	32·5	55·0	44·5

others give an additive response curve in which the cetane number rises to a maximum and thereafter decreases with increasing concentration. In these cases the additive is of low cetane number, and the increase in cetane number of the fuel with low concentrations of the additive is surprising. Similar curves have been reported for nitropropane when added to paraffinic diesel fuels.[11]

Addition of Gases to Air Intake of CFR engine

The effect of addition of various gases to the intake air of the CFR engine are tabulated in Table III. In all cases the effect of the addition of gases at the concentrations tested was small. Oxygen, nitrogen, and

methyl bromide have no effect, whilst of the gases tested chlorine and hydrogen sulphide have the greatest effect.

Addition of Compounds in Vapour Phase to Intake Air of CFR Engine

Ten compounds, previously tested as additives to the fuel, were tested in vapour-phase addition to the intake air. Results of these tests are given in Table IV. In general, the effect of any additive in the vapour phase is greater than if added to the liquid fuel. This is illustrated in Figs 2, 3, 4,

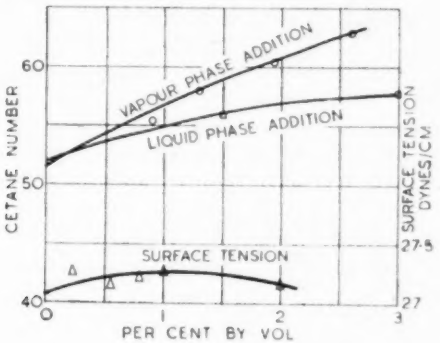

FIG 2

EFFECT OF DIETHYL ETHER

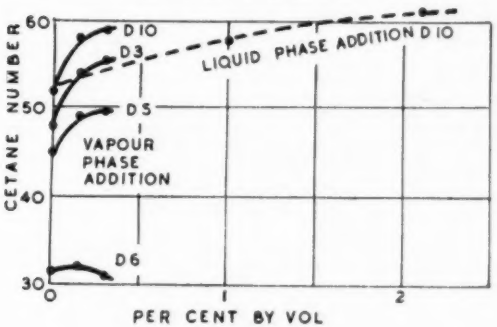

FIG 3

EFFECT OF NITROMETHANE

which compare vapour- and liquid-phase addition for diethyl ether, nitromethane, and 1-nitropropane. There is an indication in the case of nitromethane that at low concentration of 0·5 per cent by vol the effectiveness of the additive in the air stream has reached a maximum. This behaviour is also exhibited by 2-nitropropane (Fig 5) and by *tert*-butyl hydroperoxide (Fig 6).

Behaviour of Selected Additives in Crossley Single-cylinder Engine

Tests were carried out on the effect of ethyl nitrate, *tert*-butyl peroxide and diethyl ether when added in the liquid and in the vapour phase to the

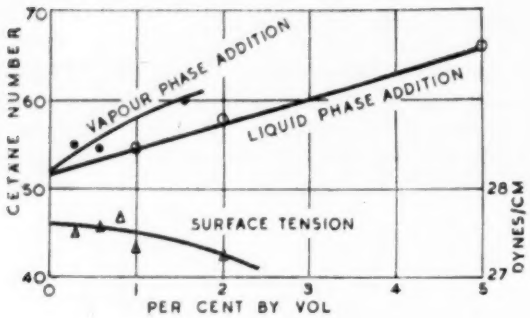

FIG 4

EFFECT OF 1-NITROPROPANE

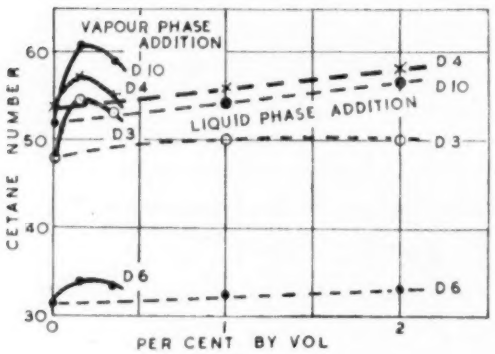

FIG 5

EFFECT OF 2-NITROPROPANE

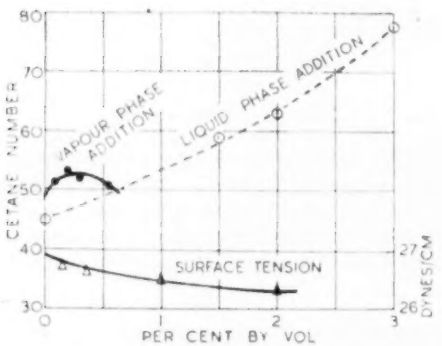

FIG 6

EFFECT OF *tert*-BUTYL PEROXIDE

TABLE IV

Additive	Concentration, % by vol	Fuel					
		D.3	D.4	D.5	D.6	D.10	D.11
Diethyl ether	0	49·0	52·5	46·0	31·5	51·5	43·0
	0·89	49·5	54·0	48·0	35·0	55·5	46·5
	1·28	52·0	54·0	49·5	36·0	58·0	48·5
	1·93	52·5	56·0	51·0	35·0	60·5	49·0
	2·00	54·0	60·5	52·0	36·0	61·5	50·0
	2·61	55·0	59·0	53·0	35·5	61·5	52·5
	3·34	58·0	61·0	52·5	36·5	63·0	53·0
Carbon disulphide	0	48·0	53·0	45·0	31·5	52·0	42·0
	0·23	50·0	54·0	46·5	32·5	53·5	42·5
	0·47	52·5	54·5	46·5	32·5	55·0	43·5
	0·71	52·5	55·0	47·0	32·5	56·0	44·0
	0·85	52·0	55·0	48·0	33·0	57·5	45·0
	1·02	53·5	55·0	49·0	33·0	58·0	45·5
Chloroform	0	48·0	53·0	45·0	31·0	52·0	42·0
	0·53	52·0	53·5	47·5	31·5	56·0	44·5
	0·93	53·0	53·5	49·5	31·5	57·5	47·0
tert-Butyl hydroperoxide	0	51·0	55·0	48·5	—	56·0	46·0
	0·07	53·0	60·5	51·5	—	61·0	48·0
	0·12	53·0	55·0	48·5	—	60·0	47·0
	0·19	54·0	57·5	53·5	—	65·5	48·5
	0·29	52·0	56·5	52·0	—	62·5	51·0
	0·54	55·0	59·0	51·0	—	61·5	48·0
Diethylene dioxide (dioxan)	0	51·0	56·0	47·5	—	57·0	46·0
	0·14	51·5	61·0	50·5	—	60·5	46·0
	0·25	53·5	58·0	47·5	—	61·5	46·5
	0·36	58·0	58·0	50·5	—	59·5	47·0
	0·45	53·5	58·5	51·0	—	59·0	48·0
	0·59	56·0	55·5	52·5	—	62·5	51·0
Nitrobenzene	0	51·0	55·0	45·0	—	56·0	46·0
	0·08	52·0	56·0	45·5	—	59·0	46·0
	0·11	54·5	58·0	51·0	—	64·0	48·5
Benzene	0	51·0	56·0	47·5	—	57·0	46·0
	0·25	54·0	60·5	51·0	—	61·0	46·0
	0·45	54·0	56·5	50·0	—	62·0	50·5
	0·81	52·5	62·0	48·5	—	60·0	47·5
1-Nitropropane	0	48·0	53·5	45·0	31·5	52·0	42·0
	0·27	49·5	50·0	43·0	32·0	55·0	41·5
	0·56	51·0	52·0	47·0	34·0	54·5	44·0
	1·53	54·5	59·0	51·0	31·0	60·0	45·5
2-Nitropropane	0	48·0	53·5	45·0	31·5	52·0	42·0
	0·16	55·5	57·5	48·5	34·0	61·0	48·5
	0·34	53·0	55·0	50·0	33·5	59·0	48·0
Nitroethane	0	48·0	53·5	45·0	31·5	52·0	42·0
	1·09	54·0	56·0	48·5	33·0	59·0	46·5
Nitromethane	0	48·0	53·5	45·0	31·5	52·0	42·0
	0·16	54·0	55·0	49·0	32·0	58·0	45·0
	0·30	55·5	58·0	49·5	31·0	59·0	49·0

test fuels using the single-cylinder Crossley engine. The results are given in Table V, and confirm the effects observed in the operation of the CFR engine.

TABLE V

Additive	Method of addition	Concentration, % by vol	Fuels				
			D.3	D.4	D.5	D.10	D.11
—	—	0	51·5	58·5	46·5	58·0	48·5
Ethyl nitrate	Liquid phase in fuel	0·25	57·0	61·5	55·0	65·0	—
		0·5	61·5	67·0	60·0	67·0	—
		0·75	63·5	70·0	63·0	69·5	—
		1·0	65·5	72·0	64·0	75·0	—
		1·5	67·0	74·0	67·0	80·0	—
		2·0	68·5	75·0	68·5	84·0	—
	Vapour phase in air	0·013	56·5	59·5	52·0	60·0	50·5
		0·024	56·5	59·5	51·5	62·0	49·5
		0·029	58·0	58·0	52·0	64·0	50·0
tert-Butyl hydroperoxide	Liquid phase in fuel	0·25	54·0	60·5	49·0	62·0	—
		0·5	56·0	—	52·5	63·5	—
		0·75	60·0	63·0	55·5	67·0	—
		1·0	63·0	65·0	58·0	68·5	—
		1·5	65·5	66·5	59·5	—	—
		2·0	67·0	67·5	61·5	70·0	—
	Vapour phase in air	0·044	57·0	60·5	51·5	63·5	52·5
		0·088	57·0	58·5	49·5	61·0	52·5
		0·111	58·0	62·5	52·0	63·5	52·5
		0·127	56·0	61·5	50·0	64·0	49·5
Diethyl ether	Liquid phase in fuel	0·5	53·5	61·0	48·0	60·5	—
		1·0	54·0	62·0	49·0	62·0	—
	Vapour phase in air	0·136	52·0	59·5	47·0	60·0	—
		0·339	53·5	60·0	49·0	61·5	—

Note: The percentage concentration of additive to fuel (by volume) when added in the vapour phase to the intake air is based on an approximate fuel consumption of 11 cc/min.

The effect of both ethyl nitrate and diethyl ether in vapour-phase addition at low concentrations is greater than the effect of these compounds when added in the liquid phase. *tert*-Butyl hydroperoxide, however, as in the case of the CFR engine results, appears to reach its maximum effect in the vapour phase at low concentrations, and thereafter does not appear to be as effective as in the liquid phase. The difficulty of obtaining higher concentrations in the vapour phase prevented a more complete study of this phenomenon, which may be due to the decomposition of the peroxide in the airstream before ignition of the fuel droplets occurs.

Effect of Fuel Characteristics of the Effectiveness of an Additive

It can readily be seen from the results quoted that the effectiveness of an additive as an ignition accelerator in a diesel fuel is directly affected by the cetane number of the " clear " fuel. In all cases the additives tested made

only a small improvement in the naphthenic oil D.6. Fuel D.10, which is the most paraffinic oil tested, is more sensitive to additives of all kinds than any of the other fuels.

When the additive is added in the vapour phase, however, the results show that the naphthenic fuel D.6 and the paraffinic fuel D.10 had a consistently higher additive response than in the liquid phase. With the other fuels containing more aromatic hydrocarbons this was not always the case.

Effect of Additives on the Surface Tension of the Fuels

The effect of an additive in the liquid phase may be due to physical as well as chemical effects. Of the physical effects an alteration in the surface tension of the fuel might influence the break-up of the fuel spray by controlling the ultimate droplet size. Moreover, the concentration of the additive at the surface of the droplet will be governed by its effect (positive or negative) on the surface tension of the fuel. The effect of the additives on the surface tension of the fuels tested was determined at all concentrations at which the additive had been used. Determinations were made using the du Noüy surface tensiometer. Some of these results are included in Figs 2, 4, and 6. In these cases the surface tension of the fuel is reduced by the additive, but the effect is small.

Conclusions

The effect of additives upon the cetane number of a diesel fuel appears to be related to the chemical character of the fuel. In particular, paraffinic fuels have a greater additive response than paraffin–aromatic fuels, whilst naphthenic fuels have a low additive response.

In general, an additive is more effective when added in the vapour phase to the intake air of an engine than when added in the liquid phase to the fuel. *tert*-Butyl hydroperoxide, and to a lesser extent 2-nitropropane, appear to be exceptions to this general effect, since in the vapour phase they reach a maximum effectiveness at low concentrations in the intake air. There is probably a connexion between the relative effectiveness of an additive when added in the vapour phase and its effect on the cold-starting behaviour of a fuel containing the same additive. Cloud and Ferenezi [12] have shown that whilst additives in the fuel may give a reduction in minimum starting temperature of 20° to 25° F, the introduction of ethyl ether in the air-intake stream will allow starting down to at least −40° F. This effect on cold starting is not a function of cetane-number improvement, since *tert*-butyl peroxide, which produces a marked improvement in the cetane number of a fuel, has little effect upon the minimum cold-starting temperature.[13] Cold starting is facilitated by additives of relatively low ignition temperature and wide range of inflammability, and does not appear to be dependent upon volatility alone.

The surprisingly small effect on cetane number produced by the addition of diethyl ether to the fuel is in sharp contrast to the marked effect on cold starting produced by this same additive in the intake air to the engine. It would appear that two different mechanisms are involved. In the vapour phase the additive contributes to the establishment of conditions suitable for auto-ignition reactions,[14] possibly by initiating pre-flame reactions

during the compression stroke. In the liquid phase, however, the additive appears in the engine only after injection, and thus has a relatively limited period in which to contribute to pre-flame reactions.

ACKNOWLEDGMENTS

Thanks are due to Messrs Trinidad Leaseholds Ltd. for grants which defrayed part of the cost of the work and for a scholarship to one of us (E.P.W.), and to Dr T. K. Hanson for helpful advice and discussion.

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PRE-FLAME REACTIONS IN DIESEL ENGINES. PART II

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IN Part I it was shown that the effect of certain additives upon the cetane number of diesel fuels partly depends upon the character of the fuel, and the additive was usually more effective when added in the vapour phase with the engine intake air than when added directly with the fuel. Some additives gave a cetane-response curve which exhibited a maximum reached at very low concentrations of the additive. Several additives which are effective in raising cetane number have little value in improving cold starting, and other additives which are of great value in improving cold starting cause relatively low increase in cetane number. This suggests that different reaction mechanisms are concerned in cetane-number improvement and cold-starting performance. In order to examine this behaviour in greater detail it was considered desirable to study the pre-flame reactions occurring in the diesel engine with selected fuels, with and without the addition of ignition accelerators.

Pre-flame reactions in engines have been investigated by analysis of the exhaust gases produced when the engine is motored,[15] or by withdrawing samples of gases from the engine at predetermined positions of the stroke. For the latter method a suitable valve is necessary. Brooks,[16] and later Withrow, Lovell, and Boyd,[17] employed a valve to examine combustion reactions in a spark-ignition engine. Drinkwater and Egerton [18] used a cam-operated and later an impact arm-operated valve to obtain samples from the combustion chamber of a single-cylinder diesel engine. These workers operated the engine at half the normal speed (*i.e.*, 600 r.p.m.) in order to obtain a sampling period of 2°–4° crank angle.

More recently, Downs, Walsh, and Wheeler [19] have described an electromagnetically operated sampling valve having an opening time of 3° crank angle. This valve was used to withdraw samples of combustion gases from a spark-ignition engine in an investigation of the reactions leading to "knock" in such engines. The gases were analysed for peroxide and aldehyde content, and the results were plotted against crank-angle position for a variety of pure hydrocarbon fuels as well as for standard fuels with various additives.

The present paper describes the construction and operation of a sampling

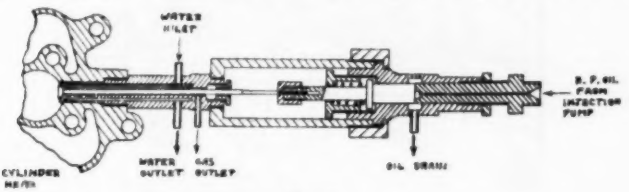

FIG 7

SAMPLING VALVE IN SECTION

valve designed primarily to suit the Crossley single-cylinder type BVD-1 diesel engine, having an opening time of 2° crank angle at the engine's normal speed (1200 r.p.m), the moment of opening of the valve being constantly variable over the whole engine cycle. Using this valve, samples have been taken from the precombustion chamber of the engine at various positions of the stroke with a series of diesel fuels. The samples have been analysed for peroxide and aldehyde content as well as for oxygen, carbon dioxide, carbon monoxide, and unsaturated hydrocarbons. The results are discussed in relation to the combustion processes, as indicated by the pressure diagrams obtained during the sampling runs. Exhaust gases from the Crossley engine and from the CFR engine, obtained during motoring runs, have been analysed. These results are compared with the results obtained by analysis of the gases drawn from the combustion chamber.

Description of Valve and Operating Gear

Figs 7 and 8 respectively show sectional views of the sampling valve and its timing gear. The external dimensions of the valve-body were controlled by the shape and size of the hole provided in the engine for the starting plug. To ensure that the pre-flame reactions were stopped as soon as the gas samples left the combustion chamber, the valve body was cooled

by means of a water-jacket formed by screwing a length of stainless-steel tube into the centre of a suitable recess in the valve body. The ends of the valve body and the stainless-steel tubes were welded together to seal the water-jacket and to form the valve-seat, which together with the valve-head was stellite faced, ground, and lapped to ensure good seating at the engine-operating temperatures. The valve-stem and its integral head was machined from stainless-steel rod and stellite faced. Clearances between the stem and the central tube of the valve body were kept to the minimum to assist in supporting the rather slender valve-stem and to ensure a high flow rate of the sampled gases up the valve.

To provide an easy, inertia-free method of opening the sampling valve and to prevent chatter of the valve on closing, an hydraulic mechanism was designed. The details of the mechanism, which was held in a suitable casing and bracket that was screwed on to the outer end of the valve body, can be seen in Fig 7. Two spindles were carried in two bearings in the casing so that they were free to move in an axial direction only, their opposing

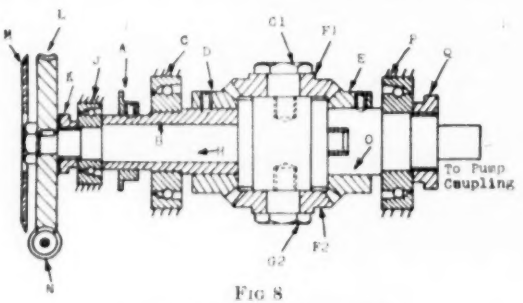

FIG 8

SAMPLING VALVE-TIMING GEAR

faces being ground and lapped perfectly square and parallel. Oil at high pressure from an injection pump was delivered to the outer spindle and passed down the central passage to the abutting faces. The flow of oil outwards separated these two spindle faces and, since the outer one was secured to the casing, the inner one moved away from it, thus opening the sampling valve. When the oil flow ceased, the inner spindle moved back to contact the outer spindle under the action of a strong spring combined with the force of the cylinder-gas pressure on the valve-head. Connexion was made at the outer end of the outer spindle for a length of injection tubing from an injection pump which was incorporated in the valve timing gear.

In order to have a clean-cut impulse of high-pressure oil to operate the sampling valve, the injection pump was run at full engine speed, thus necessitating the use of a suitable cam operated by-pass valve on the high-pressure line from the pump to the sampling valve so that the valve operated only once every two cycles.

In later experiments the injection pump was run at half crankshaft speed, the by-pass valve was removed, and the sampling valve was supplied directly from the pump. This arrangement was found to give improved

control of the sampling valve, which in this case was operated once very cycle. Control of the injection quantity, and thus the valve sampling period, was by means of a screwed adjustment on the injection-pump control rack.

The valve-timing gear was a modification of the design used by Drinkwater and Egerton,[18] and is illustrated in Fig 8. This was chain driven from the engine crankshaft, and was mounted on a bedplate fixed to the side of the main engine bed. The chain wheel A (driven from the engine, see Fig 8) was fixed to the bronze sleeve B, which was supported by the thrust ball race C and had the bevel wheel D fixed to it. This wheel drove the bevel wheel E through the two intermediate bevels F_1 and F_2 which were free to rotate on pins G_1 and G_2. These pins were screwed into the setting shaft H, which fitted in the sleeve B and was secured to the thrust

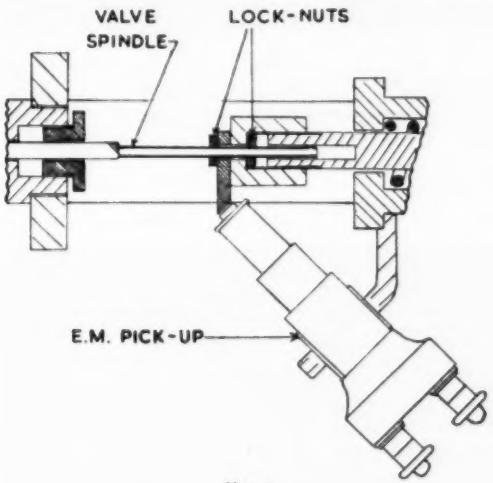

FIG 9

ARRANGEMENT OF ELECTRO-MAGNETIC PICK-UP

race J by the locknut K. The end of this shaft carried the worm-wheel L and protractor scale M, which were controlled by the worm N. The bevel-wheel E was pinned to the shaft O, which was supported by the thrust race P clamped to it by the locknut Q. The end of the shaft O was reduced to suit the injection-pump coupling.

This gear was such that the movement of the shaft H by 1° of rotation produced a displacement of 2° between the two bevel wheels D and E. That is, one degree on the protractor scale represented a change in the moment of sampling of 2° of engine crank angle. Lubrication of the timing-gear bevels and the chain drive was by means of separate oil-baths. The position and duration of the valve opening was determined by an indicating mechanism employing an electro-magnetic pick-up (Fig 9). The pick-up was mounted on the valve body as close as possible to a small mild-steel tongue fitted to the valve-stem.

Operation of the Sampling Valve

The satisfactory operation of the valve depended upon the adjustment of a number of variables.

The mating faces were adjusted periodically during sampling runs to allow for the effect of expansion of the valve-stem. The optimum setting was found to be when the faces were just touching. The return spring tension was set to give a valve opening time of 2° crank angle and was altered for each run to compensate for the change of pressure at the point of sampling. The injection-pump control rod was adjusted during sampling to give the required gas flow.

The maximum sampling rate was 30 ml/min, which involved the removal of 0·05 ml of expanded gas from the combustion chamber during every

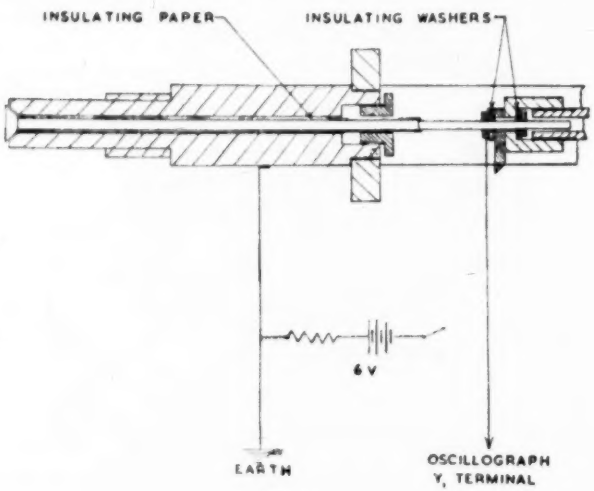

FIG 11

MAKE-AND-BREAK INDICATOR FOR MEASUREMENT OF VALVE OPENING

cycle, an operation which would be unlikely to affect the normal combustion process in the engine.

A delay of about 80° crank angle was observed between the opening of the pump delivery valve and the operation of the sampling valve due to the passage of the hydraulic pulse. This time lag was found to be constant within $\frac{1}{2}$° crank angle as shown by the sampling-valve indicator diagram for four successive openings of the valve (Fig 10).

At low settings of the pump rack, no gas flow was observed, although the indicator diagram showed valve movement over 8° crank angle. When the gas-sampling rate was adjusted to 30 ml/min, valve movement over 10° crank angle was observed. Thus it appears that the true valve opening time is the difference between the apparent opening time when sampling and the apparent opening time for zero flow, that is 2° crank angle. This zero reading is believed to be due to mechanical compression of the valve-

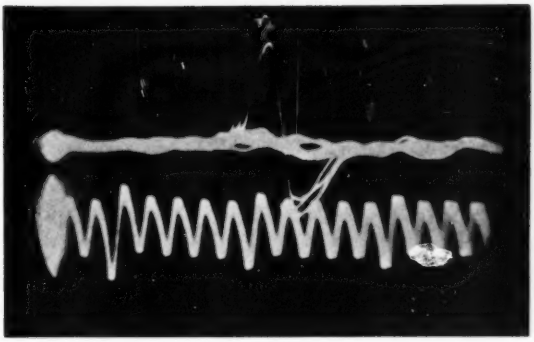

FIG 10

INDICATOR DIAGRAM TRACE FOR FOUR SUCCESSIVE OPENINGS OF THE VALVE

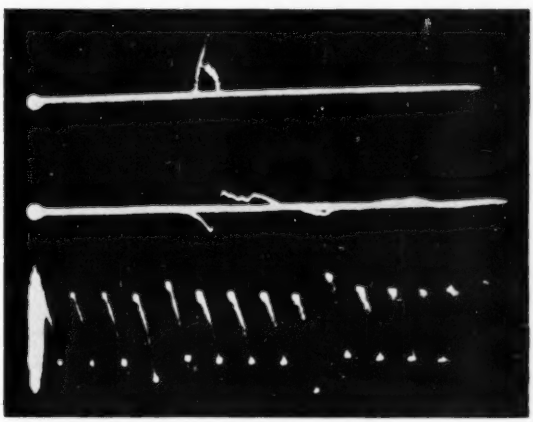

FIG 12

INDICATOR DIAGRAM FOR "MAKE AND BREAK" AND E.M. PICK-UP SHOWING VALVE OPENING TIME OF $\frac{2}{3}°$ OF CRANK ANGLE

To face p. 316.

spindle caused by a force operating at the end of the spindle and tending to open the valve against the gas pressure in the combustion chamber.

In order to check that the actual valve opening time was 2° crank angle, a special indicator was fitted to the valve (Fig 11). The head and seat formed a make-and-break contact in an electrical circuit, the stem being insulated from the valve body. The lifting of the valve did not break the circuit completely, but caused an increase in resistance proportional to the height of the peak in the indicator diagram. This is shown in the upper trace of Fig 12 and indicates that the true opening time of the valve is 2° crank angle. A rough estimate of the extent of valve lift was obtained by opening the valve manually, so that the oscilloscope trace lifted by an amount equal to the height of the peak. The extent of movement of the valve was measured and found to be 0·0004 inch. The same value was obtained from calculations based on the rate of gas flow.

Collection and Analysis of Samples

After leaving the sampling valve, the combustion chamber gases were passed through a trap cooled in Drikold and alcohol, then through a gas sampling bottle, and finally into an aspirator. After taking each sample the trap was removed from the Drikold, freshly distilled water added, and the solution was filtered to remove particles of carbon. The solution was divided into two portions for the analysis of aldehydes and peroxides.

Analysis of the Gas Samples

The gas samples collected in the sampling bottle were analysed for carbon dioxide, oxygen, carbon monoxide, and unsaturated hydrocarbons. The absorbents used were solutions of potassium hydroxide, sodium hydrosulphite, ammoniacal cuprous chloride, and concentrated sulphuric acid respectively. The analyses were carried out in a Sleigh portable gas-analysis apparatus.

Analysis of Liquid Samples

The analysis of peroxides and aldehydes was carried out using colorimetric methods, by which it was possible to estimate concentrations of peroxides and aldehydes down to 0·1 parts per million and 1 part per million respectively, for a gas sample of 1 litre.

For the colorimetric estimation of peroxides, the most suitable reagent was found to be ferrous thiocyanate, which consists of a mixture of ammonium thiocyanate and ferrous ammonium sulphate dissolved in equal volumes of ethyl alcohol and water. To remove traces of nitrogen peroxide produced in the engine during the power stroke, a small quantity of sulphamic acid was added to the sample before analysis. The sample was treated with an equal volume of the ferrous thiocyanate reagent, and the depth of colour produced in the mixture was determined with a photoelectric colorimeter. A blank determination using equal volumes of water and reagent was also carried out, and the concentration of peroxides was then determined from a calibration curve of colour depth/peroxide concentration.

The most sensitive method for the analysis of aldehydes was found to be

that employing Schiff's reagent. The reagent, which consists of rosaniline decolorized by sulphur dioxide, was prepared according to the method of Busch and Berger.[20] The aqueous sample was treated with one-sixth of its volume of reagent and the mixture placed in a constant-temperature bath and in the dark for 1 hour, after which the depth of colour was noted in a colorimeter. A blank determination using water in place of the aqueous sample was also run. A calibration curve was constructed using standard solutions of formaldehyde. This method suffers from the disadvantage that higher aldehydes give a lower depth of colour per mole than formaldehyde and therefore, when large concentrations of higher aldehydes are present, the observed values are low. For this reason the results are considered to have a comparative rather than absolute significance.

Additional Methods of Analysis Required for Motoring Experiments

In motoring experiments, which are described later, relatively large samples were obtained, and a more extensive analysis of both aqueous and oil layers was possible using the following methods.

Peroxides in the oil layer were estimated colorimetrically using a ferrous thiocyanate reagent containing ammonium thiocyanate and ferrous ammonium sulphate dissolved in de-aerated methanol. After treating the sample with the reagent and noting the colour, a blank determination was carried out using the diesel fuel. The colorimeter was calibrated against standard solutions of ferric chloride.

Peroxides in the aqueous layer were determined by the colorimetric analysis described previously. The results obtained were checked by a titration method in which the sample was added to an excess of potassium iodide, and the iodine liberated by the peroxides titrated with standard thiosulphate.

Total aldehydes and ketones were present in sufficient quantities for them to be estimated by the hydroxylamine hydrochloride method, in which the sample is treated with an excess of the hydroxylamine salt and the liberated hydrochloric acid is titrated against standard alkali using bromophenol blue as an indicator.

The analysis of formaldehyde in the presence of other aldehydes was carried out by the method due to Schryver and Wood.[21] A mixture of phenylhydrazine hydrochloride and potassium ferricyanide in strongly acid solution was added to the sample, producing a red colour, the depth of which depends on the concentration of formaldehyde. This method is specific for formaldehyde.

A colorimetric method which is unaffected by the presence of aldehydes was used for the analysis of acetone. The aqueous sample was treated with a strongly alkaline methyl alcohol solution of vanillin and allowed to stand for 20 minutes at 65° C. The depth of the resulting pink colour is dependent only upon the concentration of acetone.

Experimental Results on the Crossley Engine

In the initial sampling experiments only gas samples were collected, and these were taken over a range extending well into the flame region. The variation in composition of the combustion-chamber gases with

sampling position is shown in Fig 13 with the engine running under standard conditions (Table VI) on pool diesel oil.

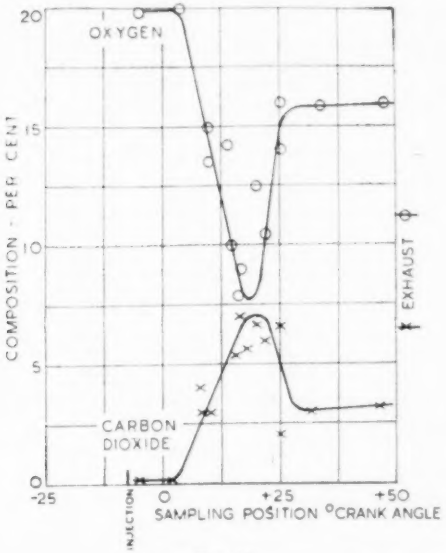

FIG 13

ANALYSIS OF COMBUSTION CHAMBER GASES, POOL DIESEL OIL

Experiments with different fuels showed slight variations in the analytical results, and it was decided to concentrate attention on the pre-flame period in the hope of detecting chemical intermediates in the combustion chamber.

TABLE VI

Crossley Diesel Engine Standard Operating Conditions

Variable	Standard condition	Tolerance
Injection timing	−8° crank angle	±½°
Speed, r.p.m.	1200	±10
Load	Full	—
Volumetric rate of fuel consumption, ml/min	41·5	±1·5
Cooling-water temperature (outlet), °C	85	±5
Intake-air temperature, °C	32	±2

Formation of Peroxides and Aldehydes during the Pre-flame Period

For the work on chemical intermediates in the pre-flame period four test fuels, namely D.1, D.4, D.6, and D.15, were chosen as representative of a wide range of ignition quality and chemical composition. A list of these fuels, together with their inspection data, is shown in Table VII.

Two series of runs were carried out on each of the four test fuels, and the results for each series of runs are plotted separately. During the first

TABLE VII

Inspection Data of Test Fuels

Description	D.1 High-cetane secondary reference fuel	D.2 Low-cetane secondary reference fuel	D.4 Scotch shale oil	D.6 Naphthenic gas oil	D.15 Fischer-Tropsch middle distillate
Sp. gr., 60/60° F	0·810	0·8795	0·839	0·890	0·756
Distillation :					
I.B.P., ° C	243	185	188	210	—
10% at	258·5	199	215·5	230	—
20% at	262·5	202	231	243	—
30% at	266	205	248	249	—
40% at	269·5	209	264	256	—
50% at	273·5	213	281·5	264	—
60% at	278	220·5	297·5	273	—
70% at	283·5	227	213	284	—
80% at	291	235	330	300	—
90% at	303	242	349	323	—
F.B.P.	349	268	362	367	—
Recovery, %	—	—	96	94	—
Flash point (P.M. closed), ° F	230	154	178	184	—
Viscosity, Redwood I, at 100° F, sec	34·0	35·6	35·0	36·0	28·8
Conradson carbon, %	—	—	0·35	0·34	—
Sulphur content, %	0·03	0·70	—	—	—
Neutralization value, mg KOH/g	0·038	0·063	0·094	2·52	0·485
Aniline pt, ° C	88·6	2·3	61·3	45·5	—
Bromine number	4·8	2·5	23·2	4·6	9·7
Chemical analysis :					
% C	—	—	—	87·1	—
% H	—	—	—	11·9	—
Mean molecular weight	—	—	—	204	—
Cetane number ASTM	70·5	18	53·5	31·5	—
Ignition delay period in the Crossley engine, ° crank angle	6½	—	7½	11	5½
Chemical composition (approx)	Paraffinic	Aromatic	Paraffinic aromatic with olefins	Naphthenic	Paraffinic

series of runs on each fuel, only low-temperature trap samples were collected. During the second series gas samples were also collected in order to determine the exact instant at which the flame front reached the sampling valve. Since the aldehyde and peroxide analyses give only comparative results, all the curves are plotted on one graph (Fig 14). A special series of runs was carried out on fuel D.6 with an injection timing of −18° crank angle in order to investigate the effects of early injection. These results are also shown in Fig 14.

Pressure diagrams have also been plotted for each of the test fuels in the following way : The rate of change of pressure diagrams were photographed, projected on to graph paper, and integrated by the method of counting squares, so giving pressure curves. The pressures at points before top dead centre were then calculated using the relationship $P_1V_1^{\gamma} = P_2V_2^{\gamma}$, where P_1 and V_1 are the pressure and volume at the beginning of the compression

stroke and P_2V_2 are the pressure and volume at a point before top dead centre; γ was taken to be equal to 1·34.

From these pressures the rate of change of pressure at a point before top dead centre was calculated, and this was used as the basis for calibra-

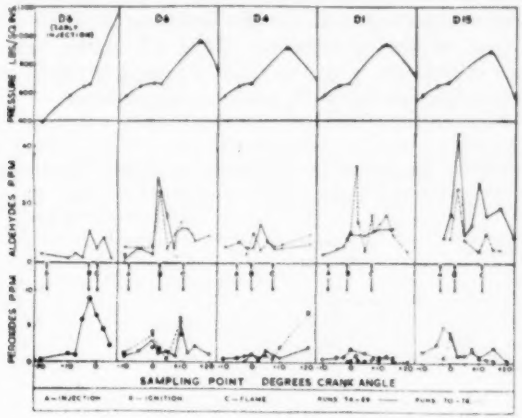

FIG 14

PEROXIDE AND ALDEHYDE CONTENT OF COMBUSTION CHAMBER GASES

tion. Although these pressure curves are not completely true, they do show accurately the points of ignition and peak pressure, and also give a comparison between the peak pressure values for various fuels.

Discussion of the Results of the Sampling Experiments

For all four fuels, peroxides and aldehydes were detected during the pre-flame period, and the general shape of the curves was comparable, but the absolute values of concentration may not be significant. It will be seen that there is a tendency for peak concentrations of aldehydes and peroxides to be associated with either the point of ignition or the arrival of the flame front at the sampling valve, and in most cases the peak pressure was associated with relatively low concentrations of peroxides and aldehydes.

TABLE VIII

Relation between Crank-angle Position and Peak Concentration of Peroxides and Aldehydes

Fuel	Degrees crank angle					
	Injection	Ignition	First peroxide peak	First aldehyde peak	Arrival of flame	Peak pressure
D.6 . .	−18	−3	−2½	−2½	+ ½	+ 9
D.6 . .	− 8½	+2½	0	+2	+11	+16
D.4 . .	− 8	− ½	0	+1½	+ 7	+12
D.1 . .	− 8	−1½	0	+1	+ 7½	+11½
D.15 . .	− 6	− ¾	−1½	0	+ 7½	+13½

In comparing the peroxides and aldehyde curves, the fuel property which gives the most satisfactory basis for comparison is that of cetane number. Although there is no correlation between cetane number of the various test fuels and concentration of chemical intermediates, there is a connexion between cetane number and the positions of the peak concentrations. Table VII shows the average crank-angle positions at which various events occurred for each of the four fuels. Table IX shows that the cetane numbers give a correlation with the times elapsing between injection and subsequent peroxides and aldehyde peak concentrations.

TABLE IX

Time Elapsing between Injection and Appearance of Peroxides and Aldehydes

Fuel	Cetane number	Degrees crank angle	
		First peroxide peak	First aldehyde peak
D.6 . . .	31·5	8½	10½
D.4 . . .	55	8	9½
D.1 . . .	70·5	8	9
D.15 . . .	—	4½	6

The behaviour of fuel D.4 (shale) was peculiar in that the peroxide concentrations were relatively low. Comparing the results for fuel D.6 (naphthenic), is seen that with earlier injection timing the delay period was longer and the peak peroxide concentration was higher. At the same time the peak concentration of aldehydes was lower.

Results Obtained with Fuel D.2 when Periodically Misfiring

It was found that when running under standard conditions on test fuel D.2 (aromatic), the engine misfired every fifth or sixth cycle. Five sampling runs were carried out under these conditions, and the results are shown in Fig 15. Compared with the results for the other test fuels, the peroxide and aldehyde concentrations were relatively high. These high concentrations may not be due to the fuel undergoing rapid peroxidation reactions. It is more probable that after each misfiring cycle the gases in the cylinder during the next compression stroke contained high concentrations of chemical intermediates from the exhaust gas. This view is supported by the presence of relatively high concentrations of aldehydes before injection of the fuel.

Aldehydes in the Exhaust Gas of the Crossley Engine

Two special runs were carried out with fuel D.1, in order to determine the concentration of aldehydes in the exhaust gas. One of these runs was carried out under standard operating conditions and the other during which the engine was idling. A third run was carried out with test fuel D.2.

The exhaust sample was passed through a series of three bubblers containing water, and the volume of gas was measured by a gas meter. The aldehyde concentration in the resulting aqueous solution was determined by the Schiff's colorimetric method. The results are shown in Table X,

TABLE X

Aldehydes in the Exhaust Gas

Fuel	Load	B.H.P.	Concentration of aldehydes, p.p.m.
D.1	Full load	6·5	1·05
D.1	Idling	0·6	3·95
D.2	Full load	6	7·7

and indicate that the aldehyde concentrations with fuel D.1 are relatively low when compared with published figures for other engines.[22] This may be due to the high cetane number of the fuel used. With fuel D.2 and operating under periodic misfiring conditions, the aldehyde concentration

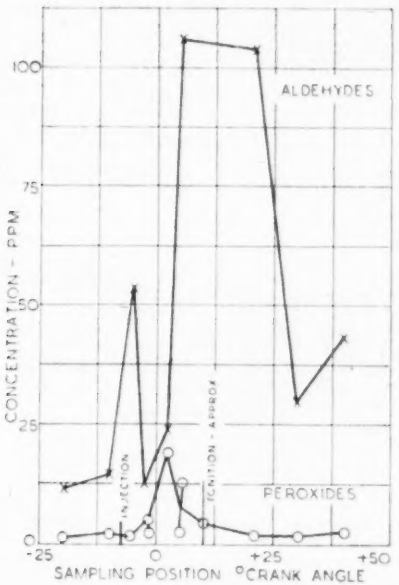

FIG 15

PEROXIDE AND ALDEHYDE CONTENT OF COMBUSTION CHAMBER GASES, FUEL D.2

was higher than with D.1 under normal conditions. It was found from the sampling runs that the concentration of aldehyde in the combustion chamber before injection was greater for fuel D.2 than D.1.

By calculating the proportion of exhaust gas not scavenged from the combustion chamber, a calculated value for the concentration of aldehydes present before injection was obtained and compared with the experimental value (Table XI). This large difference between observed and calculated values may be due to the oxidation of the hydrocarbon molecules surviving in the unscavenged exhaust gas during the compression stroke.

TABLE XI

Fuel	Aldehyde concentrations in the combustion chamber, p.p.m. :—	
	(*a*) Immediately before injection	(*b*) From the exhaust gas
D.1	3	0·03
D.2	13	0·22

Analysis of Exhaust Samples from the CFR Diesel Engine

Experiments were carried out on the CFR engine during which the compression ratio was reduced until firing ceased and large exhaust samples were taken whilst motoring the engine. In this way concentrated liquid samples were obtained, thus permitting the analyses of these samples by more reliable titration methods and extending the analysis to include chemical intermediates other than peroxides and total aldehydes.

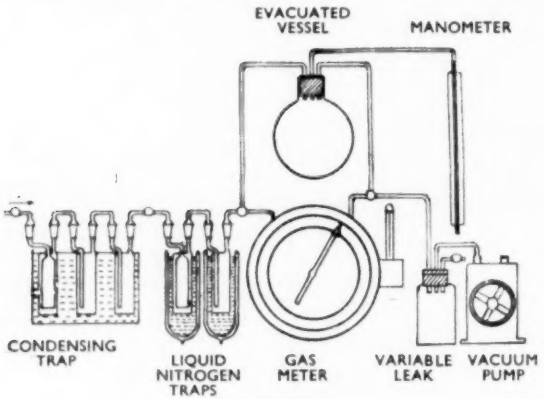

FIG 16

EXHAUST GAS SAMPLING APPARATUS

The number of runs carried out was limited to five, due to the injurious effect of large quantities of unburnt fuel on the cylinder walls of the engine. Samples were collected for one fuel at three different compression ratios and for two other fuels at the lowest of the three compression ratios.

Collection of Gas and Liquid Samples

As shown in Fig 16, the gas sample was passed through a series of condensing traps cooled in a mixture of solid carbon dioxide and alcohol and then through two traps cooled in liquid nitrogen to remove carbon dioxide and any unsaturated hydrocarbons. The volume of gas sample was measured by means of a gas meter. The gas sample was drawn through the apparatus by a vacuum pump, and the sampling rate was adjusted by a variable leak. On the completion of sampling the expansion vessel and lines were evacuated, the tap in the line was opened, and the traps lifted

clear of the liquid nitrogen, thus allowing the condensed carbon dioxide and unsaturated hydrocarbons to expand into the evacuated vessel. When the whole gas space had reached room temperature the pressure was measured and a gas sample was taken from the expansion vessel and from the traps as a check on the homogeneity of the gases in the system. Knowing the total volume of the system and the final pressure and concentrations of carbon dioxide and unsaturated hydrocarbons, it was possible to calculate the average concentration of these components in the exhaust gas. By using this technique the two components were concentrated into a smaller volume, thereby improving the sensitivity of the gas analysis.

Experimental Procedure

The engine was warmed up using the test fuel, and when the standard conditions were reached the variable compression plug was run out until firing ceased, when it was possible for the plug to be run in a short distance without firing restarting. Sampling of the exhaust gas was then started and continued until the water-jacket temperature reached 75° C and the sampling was stopped. The engine was then warmed up by running in the compression plug until firing recommenced. When the temperature reached 95° C, the compression ratio was reduced until the engine ceased to fire and sampling was continued. The volume of the sample was approximately 150 litres.

Experimental Results

The results obtained during the motoring experiments are presented in Tables XII, XIII, and XIV. It is seen from Table XIV that for the two

TABLE XII

CFR Engine Standard Operating Conditions

Variable	Standard condition	Tolerance
Engine speed, r.p.m.	900	± 6
Air-intake temperature, ° C	36	± 2
Water-jacket temperature, ° C	85	±10
Injection timing, ° crank angle	−13	—
Injection pressure, p.s.i.	1500	±50
Rate of fuel consumption, ml/min	13·0	± 0·2

TABLE XIII

CFR Motoring Runs—Experimental Conditions

Run number	Fuel	Compression ratio	Mean intake-air temp, ° C	Mean rate of fuel consumption, ml/min	Vol, cu. ft.	Gas temp, ° C	Sample pressure, mm/Hg
1	D.6	10·65	37·8	13·1	6·99	21·0	740·2
2	D.6	8·50	37·9	13·1	6·09	19·2	742·4
3	D.6	7·67	35·0	13·1	5·93	18·6	742·4
4	D.4	7·67	37·0	12·9	6·03	21·1	751·6
5	D.1	7·67	35·6	13·0	4·36	20·5	751·6

TABLE XIV

Analysis of Liquid Samples from CFR Motoring Experiments

Run no.	Analysis of oil layer. Quantities in moles × 10^{-6}			Analysis of aqueous layer. Quantities in moles × 10^{-6}					
	Peroxides	Higher aldehydes and ketones	Formaldehyde	Peroxides: Colorimetric	Peroxides: Titration	Total aldehydes (colorimetric)	Total aldehydes and ketones (titration)	Formaldehyde (colorimetric)	Acetone (colorimetric)
1	128	278	None detected	42·9	45·0	157	453	73·5	113
2	2·5	25·8	,,	0·36	—	1·2	(6·7)	(0·59)	4·2
3	1·2	26·5	,,	0·02	—	0·1	(5·0)	(0·05)	4·8
4	26·5	44·0	,,	0·72	—	None detected	—	—	3·7
5	23·2	20·3	,,	3·4	3·2	5·2	(13·4)	2·9	3·1

The figures in brackets were obtained by calculations using a factor based on the analysis for run number 1 and have only a semi-quantitative significance.

aqueous samples containing relatively large concentrations of peroxides, the results obtained by the potassium iodide–thiosulphate method and by the ferrous thiocyanate colorimetric method agreed closely. The hydroxylamine titration method for total aldehydes and ketones gave a much higher figure than the Schiff colorimetric method, even after allowing for the inclusion of acetone. This difference may be accounted for by the presence of higher aldehydes in the aqueous layer.

The relatively high figures for total aldehydes and ketones in the oil layer is evidence of the presence of long-chain carbonyl compounds during the pre-flame period.

Table XV shows the final analyses of the CFR motoring samples calculated from the concentrations given in Table XIV.

TABLE XV

CFR Motoring Experiments—Analysis of Exhaust Samples

Run no.	Fuel	Calculated temp at T.D.C., °C	Volume of gas sample, g moles	Vol of oil layer, ml	Vol of aqueous layer, ml	Concentration in the gas sample, %		Concentration in the gas sample, p.p.m.			
						Oxygen	Carbon dioxide	Peroxides	Formaldehyde	Higher aldehydes and ketones	Acetone
1	D.6	421	7·91	3·9	1·3	21·9	0·0340	22	9·3	69	14·3
2	D.6	363	8·10	4·4	1·2	21·9	0·0105	0·36	0·074*	3·2	0·52
3	D.6	343	6·88	3·4	1·0	21·8	0·0134	0·20	0·007*	3·9	0·70
4	D.4	347	7·00	2·8	1·6	21·8	0·0890	3·9	—	6·3	0·53
5	D.1	345	5·06	1·9	1·0	21·9	0·0474	5·2	0·59	5·5	0·62

All samples: Carbon monoxide: less than 0·1%.
Unsaturated hydrocarbons less than 0·0001%.

* See footnote to Table XIV.

With all three test fuels chemical intermediates were detected, and these included acetone as well as peroxides and aldehydes.

The first three runs show the effect of varying temperature on the formation of chemical intermediates. For the two lower temperatures the difference between the concentration of peroxides, higher aldehydes, and acetone was not significant, and therefore at about 350° C there appears to be little

change in relative rates of formation and destruction of chemical intermediates.

Over 360° C there was a marked increase in the concentration of all products. Increases in concentration were approximately a hundred times for peroxides and formaldehyde and about twenty-five times for higher aldehydes and acetone. The high carbon dioxide concentration at this temperature indicated that certain reactions were proceeding to the final products of combustion.

The last three runs were carried out with three different fuels at approximately the same temperature. The highest concentrations of carbon dioxide and higher aldehydes occurred with fuel D.4. D.6 gave the lowest concentration, and D.1 occupied an intermediate position. Taking cetane number as a basis for comparison, increasing cetane number was associated with higher concentrations of peroxides and formaldehyde.

Discussions

Conditions in the pre-combustion chamber of a diesel engine after the injection of the fuel are heterogeneous and complex, the larger fuel droplets persisting into the power stroke. For this reason the reproducibility of the results obtained by withdrawing samples from a limited zone in the combustion chamber is less than would be expected from a similar sampling technique in a spark-ignition engine, where the fuel–air mixture is vaporized prior to entering the cylinder. It is realized that the use of a sampling valve which on opening projects into the combustion chamber may interfere with the swirl characteristics and that despite the immediate quenching of the gases some changes in composition may take place after withdrawing the sample. The experimental data, however, show that the position in the stroke at which the peak concentrations of organic intermediates arrive at the sampling point is sufficiently repeatable to be used in discussion of the combustion reactions, although the actual amounts of the various intermediates may have only a semi-quantitative significance.

The experimental work has established that peroxides and aldehydes are formed by the reaction of the injected fuel with the hot, compressed, air and that only a small fraction of the intermediates detected are due to the unscavenged exhaust gases. When misfiring occurs with low-cetane-number fuels the peroxides and aldehydes present in the combustion chamber prior to fuel injection arise from pre-flame reactions occurring in the unscavenged fuel. There is evidence of at least two separate reaction mechanisms, a low-temperature reaction occurring during the delay period, and a high-temperature reaction occurring after ignition. During the delay period reactions occur around 350° C, resulting in the formation of peroxides and aldehydes which reach peak concentrations at the point of ignition. These are followed by reactions at considerably higher temperatures, resulting in a second peak concentration of peroxides and aldehydes. The high-temperature reactions occur after ignition, presumably while the flame is spreading throughout the fuel–air mixture, and oxidation is probably accompanied by pyrolysis of the fuel molecules. Peroxides and aldehydes are found well into the power stroke, possibly as a

result of the larger fuel droplets undergoing oxidation. By analogy with the work of Burgoyne [23] the peroxides formed during the first reaction (low temperature) may be essentially of the same chain length as the fuel molecule, whereas those formed in the second (high-temperature) reaction are probably of shorter chain length. Experimental work is now in progress to investigate this point.

The extent to which pre-flame (low-temperature) reactions occur is related to the chemical nature of the fuel. The paraffinic oils D.1 and D.15 and the naphthenic oil D.6 give higher concentrations of organic intermediates than the more aromatic shale oil D.4, but the paraffinic oils have shorter delay periods than the naphthenic oil. The reactions subsequent to ignition appear to be less sensitive to fuel quality. The motoring experiments show that acetone and formaldehyde are formed during pre-flame reactions and that some of the aldehydes formed are "higher" aldehydes.

It is well known that in starting a diesel engine at low temperatures, aldehydes are formed in relatively large amounts. Under such conditions the engine may seize due, apparently, to the formation of polymerized aldehydes and oxidation products between the piston and cylinder walls. In these cases the engine can be freed by warming. It would appear that the oxidation of hydrocarbons under cold-starting conditions in a diesel engine is characterized by the formation of aldehydes, and the extent to which such reactions proceed may determine the cold-starting qualities of the fuel. The delay characteristics in the pre-combustion of diesel fuels, however, would appear to be dependent primarily upon the formation of peroxides. The study of pre-flame reactions in petrol engines by Downs, Walsh, and Wheeler [19] has shown that peroxide formation is equally important in the promotion of knock in these engines.

The initial stages in the oxidation of hydrocarbons are the formation of hydroperoxides accompanied by formaldehyde and higher aldehydes. It has been suggested [24, 25] that aldehydes may condense with peroxides to give cyclic peroxides and hydroxy-peroxides. Under cold-starting conditions the large amounts of aldehydes present may prevent the peroxide concentration from reaching the limits necessary for auto-ignition. The experiments on motoring the CFR engine show that with rise in temperature there is a marked increase in the proportion of peroxides and formaldehyde to higher aldehydes. The delay period in a diesel engine may be dependent upon the extent to which peroxides can be formed, and this is influenced by the type of fuel used and of additive present.

The above suggestions concerning the reaction mechanisms involved in cold starting and normal combustion in a diesel engine are put forward tentatively as a possible explanation of the marked differences in performance as regards cold-starting and cetane-number improvement noted in certain additives such as diethyl ether and *tert*-butyl peroxide (Part I). Work is proceeding using an improved sampling valve which permits larger samples to be obtained and, by courtesy of the Ricardo & Co. Engineers (1927) Ltd., a second valve, of the type described by Downs, Walsh, and Wheeler,[18] will also be used. The improvements in analytical technique permitted by the larger samples will enable a more precise evaluation of the nature of the peroxides and aldehydes than is at present possible.

ACKNOWLEDGMENTS

Thanks are due to Trinidad Leaseholds Ltd. for grants which defrayed part of the cost of this investigation, for the gift of the Crossley single-cylinder engine, and for scholarships to three of us (W.E.M., W.D.R., and E.P.W.), to the Anglo-Iranian Oil Company for the gift of the Sunbury indicating mechanism and for samples of oils; to the Fuel Research Station, D.S.I.R., Greenwich, for the sample of Fischer–Tropsch diesel fuel, and to Dr A. H. Nissan, Dr T. K. Hanson, and R. Stansfield for helpful advice and discussion.

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DISCUSSION

THE PRESIDENT: I am sure you will all wish to thank the members of this Birmingham University team for the paper. (*Applause.*)

DR D. BARBY: As a chemist, I must confess to a feeling that the engine is not a suitable vehicle for carrying out measurements of a high order of accuracy, but the results quoted in Table II, for example, speak for themselves in this respect. I have also long felt that the engine is an apparatus in which chemical reactions take place: only differing from a retort, say, in that there are rather more variables and rather less control. It is pleasant, therefore, to find that chemists have in fact been studying what is happening in this particular retort, and relating their results to fundamental ideas.

Turning to the papers in detail, and to Part I in particular, I was struck by the amount of work which had gone into the effort to evaluate additives as cetane number improvers. It is unfortunate that the results tell us little that is new; but they are a valuable confirmation of what other workers have found. This is, of course, no detriment. It seems to me that these additives should be rated against test fuels D.6 and D.11. I am under the impression that fuels of cetane numbers of 50 and over are in little need of improvement, and therefore, that we must consider only fuels which have a cetane rating less than about 50. When this arbitrary restriction is made it becomes obvious that the two most important additives are *tert*-butyl hydroperoxide and iso-amyl thionitrite, for these are the only ones which affect the ratings of the two low-cetane fuels. The improvement of fuels in this respect is, of course, a matter of some moment

in, to quote one instance, the U.S., where fuels of rather lower cetane number are quite common and there is a railroad specification for diesel fuels which calls for a cetane rating of 40 minimum.

In Table III we find the effect of gases added to the air stream, and these appear to have little effect.

The maxima in the concentration–cetane number curves observed when improvers are added in the air stream brings to mind the effect of heating the air intake of a diesel engine when carrying out cold-starting tests. There is a fairly critical temperature region in which cold starting can be brought about. This has been ascribed to the possibility of having too weak a mixture at the upper temperatures, and one wonders whether this idea of too weak a mixture might not account for the optimum concentration observed. There is also another possible explanation, which may be of interest : If there is too high a peroxide concentration in a system, the peroxides start to break down of their own accord. Supposing that this was to happen before pre-flame reactions set in, then there would be no improvement in the rating of the fuel, accounting again for the maximum observed. I have no idea whether either of these ideas is correct, but I suggest that they may be worth considering.

I am not too happy about the surface-tension measurements that have been made. Although the authors do not say so, I imagine from the fact that a du Noüy tensiometer was used that the temperature of measurement was about 20° C. If so, these results would be of rather more significance had the measurement been carried out at a temperature more nearly approximating to that inside the combustion chamber during injection. As it happens, atomization tests have been carried out on water and on water to which a wetting agent was added to reduce the surface tension to about 20 dynes/cm. This was done by measuring the droplet-size distribution over the spray, and there was no significant difference noted. But in any event, this is a very minor point indeed.

The effect of ether on cetane number was small : surprisingly small to the authors; but is this so astonishing? In the one case materials are added which facilitate the formation of peroxides and other intermediates; in the other case the desire primarily is to improve the volatility. There would be little point, for example, in improving the ignition quality of a fuel of Cetane No. 50 to facilitate cold-starting if the fuel, or some of it, could not be volatilized first. In other words, however good the ignition quality of a fuel is at low temperatures, that fuel will not burn unless some of it is made volatile—and I suggest that the use of ether as a cold-starting aid is to assist as a result of the thermal effect of its combustion in the vaporization of the fuel, rather than to contribute to or catalyse pre-flame reactions despite its own Cetane No. of about 110. The authors suggest that there may be two mechanisms involved when considering cetane improvement and cold starting : it would be of interest to have further details of their ideas in this respect, because cold starting is a problem which is likely to become more acute as the sub-arctic regions are more widely used.

To conclude my remarks on Part I, it does seem somewhat sweeping to generalize that naphthenic fuels have a low additive susceptibility on the basis of tests carried out on only one naphthenic fuel (D.6), and I feel it to

be premature although not necessarily incorrect to extrapolate from one result to all fuels of this nature.

Turning now to Part II, I have a query to make about the analytical methods. In the analysis of liquid samples it is stated that sulphamic acid was added to the water to remove nitrogen peroxide. The question is, when? If it was added before peroxides were admitted there is no bother, but if it was added afterwards, one wonders what the reproducibility of the method was; for N_2O_4 decomposes peroxides very rapidly.

Fig 13 is interesting in describing a test carried out on the sampling technique using "Pool" diesel oil. On the power stroke, all valves are closed, and this prompts one to wonder where the oxygen has come from and the CO_2 gone to after about 20° crank angle. In this time, about 2·8 m.sec, the volume of the system has increased by roughly 10 per cent, and so the effect cannot be a fortuitous mathematical one. The curve gives more of the impression of a shock wave passing the sampling point, and as the swirl rate in the Mk. II Comet head is, according to Ricardo and Co., about ten times the engine r.p.m., in 36° of crank angle the gases will swirl once. When viewed in this light, it seems as though the analysis is of the gases at a point when a combustion region approaches and passes that point. If this is a correct explanation—and the views of the meeting would be of interest in resolving this—then it appears that the system is heterogeneous. Assuming that this is so, the reproducibility of the method must be somewhat low: for one cannot, for example, analyse the portion of this room where the rostrum is and finding that the rostrum volume concentration is 50 per cent, say that the rostrum concentration of the whole room is also 50 per cent. Put that way, it sounds silly; but in unfavourable conditions that is what the sampling of a heterogeneous system comes to. I have no doubt, however, that a much more convincing explanation of the meaning of the sudden rise in oxygen content can be put forward.

I can suggest for consideration a possible explanation of the low peroxide concentrations of fuel D.4. Olefins react with peroxides, and so do aryl amines. The bromine number of this fuel is high, and hence presumably so is its olefin content. Moreover, shale oils have often a high nitrogen content. Further, the fuel is also aromatic; and aromatics may act as inhibitors of peroxide formation.

The aldehyde formation referred to in the cold starting of diesel engines may well be a slow-combustion phenomenon. One can visualize peroxide–aldehyde and other complexes of aldehydes being polymerized to form this well-known deposit, which looks like cylinder lacquer, but which, on warming, turns into a dirty black oil. Since I have mentioned cylinder lacquer, it might be of interest to hear any comments on lacquer formation, as some people believe that this also can be partially at least attributed to pre-flame reactions.

Finally, considering the more mundane details, further data would have been welcomed. A number of tables are very incomplete. Table VII, for instance, has little value to the chemist as it stands; but the filling in of gaps and the addition of measurements such as refractive index, aromatic content, and perhaps nitrogen and oxygen contents; together with a group analysis, such as either Waterman's or better still the n.d.M. method, it would be of the utmost value in comparing experimental results

with fuel characteristics. Aromatic content is here specified in addition to hydrocarbon group analyses because these have been known to give zero aromaticity values in cases where the direct determination gives a positive aromatic content. The engine data might have been expanded also. One calculates that the full load for the Crossley mentioned in Table VI is about 93 m.e.p. at 1200 r.p.m. (from the maker's data of 10 h.p. at 1500 r.p.m.), and estimates that the fuel consumption quoted in Table VI applied to a load of 40 to 45 m.e.p. Confirmation of these points would have been interesting.

Professor Garner : The question has been raised as to why we carried out tests on additives with diesel fuels of cetane numbers of over fifty which are higher than are required for marketing. In our experimental work to investigate the effects of additives, we required a wide range of cetane numbers in order to determine those effects. That is why one of the fuels was a Fischer–Tropsch gas oil of high cetane number. The question of the effect of interfacial tension and surface tension on droplet size is not simple, and there are many references in the literature showing that, under some conditions, lower surface tension increases droplet size and under others lowering surface tension decreases droplet size.

There appears to be very little reference in the literature to lacquer formation, which is often found in low-temperature diesel operation : it may result in seizure between the piston and cylinder walls. Lacquer formation may also occur with gasoline engines, as when, for example, small amounts of ethylene glycol from the water-jacket leak into the engine.

W. D. Reid : The samples taken from the valve were collected in low-temperature traps which were cooled in Drikold. As soon as the trap was removed from the Drikold, distilled water was added and followed immediately by sulphamic acid. The contents of the trap were at a temperature of about -80° C and, as soon as they warmed up, the sulphamic acid dissolved in the water ; oxides of nitrogen were thus withdrawn immediately. There should therefore be very little reaction between the oxides of nitrogen and the peroxides present.

Dr D. S. Petty : I have a foot in both camps, because, although I have made a few comments to the authors on their ideas, I do not have to bear responsibility for the paper.

The opening speaker has said that he would like further details of the two reaction mechanisms. I am not quite certain whether or not the authors will agree with me, but I would not look upon the reaction mechanism operative during cold starting as completely different from that operative under normal running conditions. There is the same fundamental mechanism, but the effect of the different conditions will be to give prominence to specific reactions. During normal running there is some doubt whether the cylinder wall can influence the oxidation reactions, although the published literature is still not conclusive on the subject. However, when starting from the cold the engine will be turned over relatively slowly compared with normal running conditions, and it is probable that

the wall surface will be able to play a part in the reaction mechanism. Everything is then favourable for the condensation reaction between aldehyde and peroxide which the authors suggest. The adiabatically heated gas into which the fuel has been injected is in contact with the cold cylinder wall, and other workers have already suggested that the condensation of aldehyde and peroxide is a heterogeneous reaction similar to the polymerization of formaldehyde which is known to occur very readily in the presence of a cold surface. In other words, aldehydes are brought into a prominent role at low temperatures by reason of the aldehyde–peroxide condensation reaction.

The effect of ether on cold starting and cetane rating was mentioned. It is certainly true that when added to a fuel it might function by improving volatility during cold starting, but there is also an alternative explanation. In the engine ether will really react with oxygen to form what is presumably a rather unstable peroxide. Under starting conditions, oxidation of the fuel will be promoted when the peroxide molecules break down. On the other hand, at the higher temperatures encountered during normal running the peroxide breakdown may occur too early in the cycle to be really effective. As an extreme example, if ether is added to the intake air during an experiment under normal running conditions it will probably react almost completely before the fuel is injected.

Perhaps I may digress at this stage to mention another possible explanation of the difference between certain additives as regards their effect on cold starting and cetane rating. The ease with which the additives break down is certainly important; but it also appears to me that in some cases the difference may be related to the effect of the additives on the high-temperature or low-temperature oxidation reactions, in the same way as Dr Walsh and his colleagues have explained the effects of certain compounds on the reactions concerned with knock in spark-ignition engines. Assume that during normal running the temperature level in the cylinder is such that high-temperature oxidation reactions occur; then additives affecting these reactions will have an effect on cetane rating but not on cold starting in which low-temperature oxidation reactions will come into prominence. This may explain why certain nitro compounds do little to improve starting behaviour when added to a fuel, but are effective in increasing cetane number. These compounds probably decompose to give nitrogen peroxide, which is known to promote high-temperature oxidation reactions.

It may be objected that, under the pressures existing in the diesel engine, the low-temperature oxidation range is probably shifted up to temperatures which occur in normal running. However, even if this is so, the nature of the low-temperature ignition process is such that there is a similar explanation for the difference between additives. During the delay period preceding low-temperature ignition the reactions take place in two stages, and the second-stage reactions are similar to those that occur during oxidation in the high-temperature region. Now it has been shown by some German workers that, as temperature increases, the first delay period decreases very rapidly, whereas the second delay period increases slowly. Therefore, the additives affecting high-temperature oxidation reactions, and hence the second delay period will have a more marked effect on ignition delay under normal running condition than when starting from the cold.

J. D. BODDY : I do not think that as much information has been obtained from the results given in Part I as might have been had they been presented in a form that would have permitted easier comparison. Different quantities of the different additives were used in the tests, and little or no attempt has been made to present the results in such a way that the effects of the additives can be compared. Furthermore, I do not think that presentation of results on a volumetric basis enables a really scientific comparison to be made, particularly as some additives have gravities twice the value of others, *e.g.*, diethyl ether, sp. gr. 0·7135; chloroform, sp. gr. 1·498.

The authors have considered surface tension as a possible variable, introduced by mixing additives with the fuel, which might influence ignition delay by altering droplet size. It might also be postulated that changes in viscosity and density of the fuel by inclusion of additives would also influence atomization and quite possibly the injector delivery characteristics. It has been shown that air density will influence spray penetration*; cannot then injection of the additive into the air in vapour form have some purely physical influence on the ignition delay ?

On closer examination of the inspection data of fuel D.6, I would question whether it is true to describe it as naphthenic. The low diesel index based on the inspection data in Part I, *i.e.*, sp. gr. 0·890 and aniline point 45·5, would suggest that it contains a considerable quantity of aromatic material. Whilst the sp. gr. given for this fuel in Table VII, is more in keeping with a fuel described as naphthenic, the carbon percentage given as 87·1 is more appropriate to a gravity of 0·89 or even higher and hence a high aromatic content.† This is of some considerable importance because the results as presented do suggest that naphthenes are worse diesel fuels than aromatics. This is contrary to normal laboratory experience as well as to fundamental work, which has shown that cyclic paraffins are similar in their reaction rates to paraffins and also that S.I.T. of naphthenes are little higher than those for paraffins. Unless the authors can present some convincing evidence that D.6 is fairly described as naphthenic, I would suggest that it is more probably a mixed paraffin–naphthene and aromatic fuel with probably more aromatics present than in the fuels described as paraffinic and aromatic, which from their aniline points are not likely to be very aromatic.

I am not convinced by the statement that " when additive is added in the vapour phase, the results show that the paraffinic fuel D.10 and naphthenic fuel D.6 had a consistently higher additive response." All the liquid additives to D.6 which gave a good response, *i.e.*, nitro-benzene, *iso*-amyl, thionitrite, and *tert*-butyl hydroperoxide were not tried in the vapour phase and with the other additives, apart from diethyl ether, it is difficult to say that they had any real effect either in the liquid or vapour phase. In respect to D.10 with butyl hydroperoxide additive it is questionable whether an improvement of 5·5 Cetane No. with 0·59 per cent additive is better than 14 Cetane No. improvement with 1·5 per cent additive. Since it was not possible to add greater quantities of vapour comparable to the liquid quantities added, why were not smaller quantities of liquid additives

* Rottroch and Waldron. N.A.C.A. Tech. Note No. 299. Nov. 1931. March and Waldron. N.A.C.A. Tech. Note No. 465. July 1933.

† Howes and Rampton. *J. Inst. Petrol.*, 1949, **35**, 419.

used so that direct comparison between equivalent quantities of liquid and vapour could be made? This would have proved or disproved the interpretation of the result given in Figs 5 and 6. Would the authors agree that 1 per cent vapour addition of 2-nitropropane to D.10 would depress the Cetane No. by approximately 10 numbers, which I have derived by extrapolating the vapour-phase curve for D.10 in Fig 5? Is it not just as reasonable, if not more so, to conclude that the experimental points for vapour-phase additions belong to the same relationship as those for liquid additions? Fig 6 is even more questionable, since the neat fuel in the vapour-test tests has a Cetane No. of 48·5. Correcting the two sets to the same base would bring all points into the liquid-phase relationship within a very small error margin. I would suggest that the only difference between vapour and liquid addition of additives are the small effects of the physical differences which I have suggested earlier.

In the conclusions of both parts of the paper greater emphasis has been given to the statement that ethyl ether gives substantial improvement in cold starting, whereas butyl hydroperoxide does not, but is nevertheless the better cetane improver. There is no experimental evidence in this paper to prove this point.

On reference to the work of Nelson and Snolak, butyl hydroperoxide has only been tried in the liquid phase. Might it not prove effective for cold starting in the vapour phase? I would therefore suggest that differences between cold starting and cetane improvement with different additives are due to physical differences of volatility and latent heat and not due to essentially different chemical mechanisms as suggested.

It does seem evident that peroxides are the key compounds promoting the ignition of diesel fuels, whilst aldehydes, or at least some of them, inhibit ignition. Cullis and Hinshelwood * give some useful information on this point showing that formaldehyde has a very pronounced inhibiting effect on oxidation, whilst higher aldehydes have little or no effect. It is also worth noticing that Newmann and Aivazov † have observed that in experiments with *n*-pentane peroxides as well as aldehydes reach peak concentration just before the onset of cool flame. Correlating this work with the results presented in Fig 14 suggests that ignition in a diesel engine is associated with cool-flame ignition limits. It is significant that few aromatics show indications of cool-flame ignition limits which would explain the lower Cetane Nos. of aromatic hydrocarbons. A thorough survey of fundamental work carried out on cool-flame studies would, I believe, throw considerable light on the problem of diesel ignition and probably suggest the more suitable types of additives for different types of fuels. The indications are that an additive must: (*a*) itself be a peroxide; (*b*) react at low temperature with a fuel compound to produce a peroxide, or (*c*) inhibit the formation of formaldehyde and possibly other aldehydes.

DR E. P. WRIGHT: With regard to the comparison of the additives by weight instead of volume, we feel that that would not have a great deal of effect on our results, and the general accuracy would not be improved by correlation of the nature suggested.

* Cullis and Hinshelwood. *Faraday Soc. Discn.*, 1947, **2**, 1947.
† Newmann and Aivazov. *Acta physicochim U.R.S.S.*, 1936, **4**, 575; 1937, **6**, 279.

As to the figures showing the difference between the vapour and liquid phases, for instance, as in Fig 6, the differences were shown on several occasions. We took precautions in ensuring that the tests were carried out on all the concentrations in long series of runs without stopping, and we feel that by doing that we have offset random day-to-day variations. In many cases the tests have been repeated as many as seven times, and all the additives have given at least the same shaped curves, if not the same absolute evaluation of Cetane No.

The question as to whether additives have purely a physical rather than a chemical effect is, of course, one for discussion. We do hope that, when these techniques are fully established, we shall be able to evaluate these factors.

W. T. Lyn : The authors have rightly emphasized the difficulty in obtaining consistent Cetane No. as is borne out by test results which recorded a day-to-day variation of 3 to 4 numbers for the same fuel with no additive. It is therefore proper to compare values obtained in a single day's run as they have done. However, the conclusions will be more convincing if the table includes the successive values carried out in a day for the same fuel without additive. The variation of Cetane No. with nitrogen addition is 3 for D.6, and the authors considered it as having no effect. The variation of Cetane No. with benzene addition in fuels D.5, D.6, and D.11 are 2·5, but in this case the authors pointed out the significance of the increase in Cetane No. at low concentration of addition, and thereafter the decrease with increasing concentration. Is there any reason for the difference in the treatment of these two sets of data ?

The Cetane No. is a practical measure of ignition behaviour of fuels in engine, and as such it serves the purpose, since in practice one cannot notice the difference in engine performance from variation on Cetane No. within the limits of reproducibility. However, for fundamental study of the mechanism of ignition, as was the purpose of the present paper, it is wondered whether a more simple and better controlled laboratory method, such as an improved bomb test, could be employed to advantage.

The heterogeneous nature of combustion in a diesel engine is well known, and is one of the biggest handicaps to the investigators in this field. However, the authors have shown that in spite of this difficulty, the average state of affairs can still be assessed, particularly in the pre-flame period when pressure and temperature gradients in the chamber are comparatively small. Evidence was given that at least reaction leading to ignition is of the low-temperature mode. The pressure measurement was integrated from the rate-of-pressure-change curve, obtained by an electromagnetic type of pick-up. If a capacity or piezoelectric pressure pick up were used, I think the authors would find that immediately after the first pressure rise, the pressure curve will be superimposed with a low-frequency fluctuation of the order of about 1100 c.p.s. for the type of engine used. The amplitude of the fluctuations could be as large as 100 p.s.i. It is interesting to note that occurrence of the second peroxides and aldehyde peaks, as shown in Fig 14, would possibly fall in with the second peak of the pressure fluctuation. Would the authors consider this a point worth looking into ?

In Fig 14 and Table VIII the term " flame arrival " was used without

strict qualification. If it is assumed as the point of rapid change to CO_2 curve, would the authors then consider the lapse between the ignition point, *i.e.*, the point of rapid pressure rise, and this latter point as the time required for the earlier charge to move to the sampling valve? At the ignition point, somewhere in the combustion chamber, fuel must be ignited with rapid formation of CO_2 locally; but as the pressure propagation is at a much higher speed than the mass movement, a lag will be observed between the two events as recorded at the sampling point. This lag is seen to be the shorter the higher the rate of pressure rise, which is to be expected. Such consideration brings home the thought that, broadly speaking, it is easier for one to follow the history of a particular portion of the charge by stroboscopic sampling in a petrol engine than in a diesel engine, particularly in the case of the swirl-chamber engine, where the order of charge movement is considerable. Here stroboscopic sampling may rather present a picture of successive portions of the charge that pass through the sampling point. It is well to bear this in mind while studying Fig 14 and Table VIII.

In run No. 1 of the motoring test on the CFR engine, the compression ratio was 10·65, and there were large increases in peroxide and aldehyde concentrations in the exhaust. From our experience at BICERA, and from many recent publications, this corresponds to the region where it is possible to have a weak explosion—sometimes inaudible—accompanied by blue flame. Did the authors notice this in their trial, and was the combustion observed through a window? There may be a correlation between the two events.

It may be pertinent to mention here very briefly some earlier works at BICERA which bear close relation to the authors' findings and lend support to some of the conclusions drawn. There were in the published literature ample indications of the close relationship between such phenomena as knock in a petrol engine and the slow oxidation leading to ignition as studied more fully under steady flow conditions in the laboratory. In both cases the earlier products of reaction, such as peroxides and aldehydes, play an important part. Since factors favouring knock in the gasoline engine also improve the ignition in the diesel engine, it is very likely that these reactions follow the same course at least up to the point of ignition. The presence of such active intermediate products of combustion arising from slow oxidation would be expected to influence greatly the ignition in a diesel engine. This has been demonstrated by introducing part of the fuel of the higher or any paraffinic fuels for that matter, with the intake air. The amount admitted was well below the inflammable limit, say 10 per cent c.c.m., so that the lean mixture only underwent slow oxidation near the end of the compression stroke. This greatly assisted the ignition of the main fuel so that smooth operation was obtained from fuels ranging from 2·5 to 100 Cetane No. and covering a wide variety of chemical composition with approximately the same delay period. This lends good support to the view expressed by the authors that ignition of paraffinic fuels in diesel engine is of the low-temperature mode, and explains also the large amount of intermediate products found following the misfiring stroke and in over-fuelling under starting conditions.

A full account of this work, embodying both the theoretical and practical

aspects of the effect of fuel addition into the intake air in a compression ignition engine, will be published later.

W. D. REID : As to the CFR engine, firing was detected audibly, and it is possible that some flame might appear without any knock in the engine being heard. In the case of run No. 1, in which the compression ratio was 10·65, the carbon dioxide concentration in the sample was only 0·034 per cent, which points to the absence of flame.

A. L. WALCHAL : I appreciate the engineering ingenuity displayed in the design of the sampling gear, which in itself is an appreciable asset to diesel research.

In their paper the authors describe the trapping method of peroxides and aldehydes in the Drikold-cooled vessel; to which " freshly distilled water was added and solution was filtered to remove particles of carbon." The fact that carbon appeared in this sample is probably more significant than the occurrence of hydrocarbon peroxides. This, together with other observations, suggests to me that some chemical breakdown of the fuel similar in character to cracking does occur before oxidation takes place. Product of such breakdown is a wide range of light hydrocarbons and free carbon (which incidentally is no less a nuisance in oil-refinery cracking plants than in diesel combustion). This tendency seems to be stubbornly overlooked by diesel investigators.

Both factors upon which the appreciable rate of cracking process depends, namely the temperature and the time, are particularly well satisfied in the pre-chamber diesel. Landen * has calculated from data of Geniesse and Reuter that an appreciable quantity of gas oil can be cracked in a diesel pre-chamber, and it was actually demonstrated by Landen absorption spectra that a carbon precipitate appears at the onset of inflammation.† Yellow-white (black body) radiation characteristic of combustion preceded by thermal decomposition of fuel was observed in diesel combustion chambers by earlier investigators.‡ Direct oxidation would rather be manifested by CO_2 and CO radiation and a blue flame.

Fine carbon particles were separated at Sunbury from a lightly loaded Crossley engine exhaust gas otherwise quite free from incomplete combustion products such as carbon monoxide. Reference to this type of carbon in exhaust has been made by Drinkwater and Egerton.§

Carbon content in partly loaded diesel exhaust can be appreciably influenced by change of injection timing alone.‖

As we know peroxides of hydrocarbons of the gas oil range such as, *e.g.*, cetane peroxide, are insoluble in water, yet the description of trapping method implies that the authors dealt solely with the water-soluble peroxides. Could it not be concluded from this that pre-flame oxidation affects hydrocarbons which result, in fact, from the thermal decomposition of the original fuel. The suggestion in this discussion that a portion of peroxides formed in diesel pre-chamber are of the same chain length as fuel

* SAE Preprint 292, Jan. 1949.
† *SAE Trans.*, Jan. 1949.
‡ *Chem. Rev.*, 1938, **22**.
§ *Proc. Inst. Mech. Engrs*, 1938.
‖ *Gas Oil Pwr*, Oct. 1950.

hydrocarbons is in contradiction to the adopted method of their extraction as in distilled water, in which such peroxides would not be soluble.

The authors do not mention whether besides partially oxidized compounds any hydrocarbons were also trapped in Drikold-cooled condensers. In view of the fact that light hydrocarbons C_1 to C_5 of paraffinic type, mono- and diolefins, aromatics along with acetaldehyde, acetic acid and acetone, were found by mass-spectrometric analysis in a much later stage of diesel cycle,* it is to be expected that compounds of the similar character would be present in early stages of fuel combustion.

I would like to know how the authors arrived at a temperature of 350° C for the first phase of fuel oxidation, when the compression temperature itself in a Crossley engine is about 600° C.

As I understand, aldehydes and organic acids are the products of arrested combustion, whilst peroxides are essentially chain carriers, and in my opinion linking these together is not the thing which clarifies the outlook on the pre-flame reaction in diesel engines.

W. D. Reid : As regards the presence of carbon in the samples, it appears mainly when we are sampling at a point near the arrival of the flame; and it seems quite feasible that carbon will be formed when the flame comes near to the valve. However, cracking does not appear to occur during the early part of the delay period, and this is borne out by the fact that no unsaturated hydrocarbons were detected during the delay period in any of the runs.

On the question concerning the temperature being 350° C for the first phase of fuel oxidation, the figures were obtained from the CFR engine experiments, in which very small quantities of chemical intermediates were detected at 350° C, but large quantities were detected at 420° C. The temperatures during the delay period in the Crossley engine were approximately 460° C. The concentration of organic peroxides in the aqueous samples was of the order of 10^{-5} molar. At such concentrations all peroxides would be soluble in distilled water.

W. Penzias : I should like to address a question to the engineer of the Birmingham team. Having made the commendable move away from the CFR engine, what was the reason for using the engine that was chosen for this work in preference to a direct-injection engine?

Dr E. P. Wright : It was mainly a question of availability, since the pre-chamber engine was already there. We tried to get a direct-injection engine, but very few engines are easily fitted with both sampling valves and pressure recorders.

N. P. W. Moore : This contribution to diesel research interests us very much at the Imperial College, because it is so much an extension of the early work of Drinkwater and Egerton. It is also interesting that in the discussion of their 1938 paper to the Institution of Mechanical Engineers, J. F. Alcock suggested using a fuel-injection pump as a sampling valve.

In the paper the authors state that they propose to adopt the electro-

* *Proc. Wld Petrol Congr.*, 1951, **VII**, 280.

magnetic valve for further work, because thereby they can obtain larger samples. Is that the only reason for its adoption? The question is asked because hydraulic systems seem to have certain advantages in the facility they offer of development from normal engineering parts. Do the authors really feel that the hydraulic system cannot be developed any further?

The sampling technique in connexion with an engine can be used for studying combustion products and hence the course of reaction. Perhaps this is a case where a piece of engineering apparatus is having quite considerable significance in chemical research. There are cases, of course, in which gaseous additions to the air and their effect on diesel ignition processes are of particular interest. An instance of this is dual-fuel operation of gas engines. Another example is the operation of engines underground, where small traces of additives may be present in mining atmospheres, these additions can have a major effect on the nature of the exhaust products.

In the case of dual combustion, we have investigated at Imperial College a very wide range of what we will call the additives, compositions ranging from zero concentration to a concentration beyond stoichiometric. This work shows very clearly that we are dealing with two mechanisms of combustion. At low concentrations the additive reaction is clearly a slow oxidation reaction, and at higher concentration the reactions are of the propagated variety. Using this dual-fuel combustion system, it seems that we can promote considerable combustion with mixtures far richer than the classical upper limit under pre-mixed conditions. In that region unsaturated hydrocarbons are found in quite considerable quantities.

The importance of the time factor has been emphasized in additive reaction. In the case of diethyl ether it is known that a complete oxidation process can take place at quite low compression ratios; thus cold starting may be more dependent on the direct thermal influence during the compression stroke in the normal combustion period than on promoting ignition by providing partial oxidation products as additives.

In regard to the figures in the paper showing indicator diagrams and gas analyses, I would like to ask the authors where the indicator diagrams were taken, were they taken in the main cylinder space or in the "Comet" swirl chamber?

DR E. P. WRIGHT : The pressure readings were taken from the main chamber in a position diametrically opposite the port of the pre-combustion chamber.

The main reason for the change-over of valve was purely to obtain a larger sample of gas. It has been one of the problems of the ignition technique to deal with the small quantities involved, and the hydraulically operated valve proved incapable of giving larger samples, which meant operating the engine for rather longer periods than were desirable from the point of view of keeping the engine in proper condition.

F. L. GARTON : Chemical analysis of cylinder gases withdrawn through a sampling valve has been used to a fairly considerable extent in the investigation of the reactions which occur in the cylinders of a petrol engine. Techniques of this kind have, however, found much less application in the case

of diesel-engine combustion, perhaps because it was felt that in this case pre-flame reactions were of relatively less importance. M. G. Fiedler,* for example, ascribed knock in diesel engines to hydrogen from cracking of the fuel. The authors' sampling experiments, on the contrary, seem to show that pre-flame reactions play at least an important part.

In describing their apparatus the authors mention that a copper-gauze cylinder was fitted inside the mixing chamber as a flame arrester. Copper is a particularly active oxidation catalyst, and it might be as well to make certain that this had no effect on the results.

The statement that the effectiveness of an additive as an ignition accelerator is directly affected by the Cetane No. of the base fuel is perhaps open to question. In Table II, for example, the effectiveness of *tert*-butyl hydroperoxide is not in direct relation to the Cetane No. of the base fuel. Then again in Table V, fuels D.4 and D.10 have the same Cetane No., but ethyl nitrate in the liquid phase is considerably more effective in D.10 than in D.4. If " chemical composition " were substituted for " Cetane No." in the sentence quoted, much less exception could be taken to the statement; it appears from the next sentence that this may in fact be what the authors intended to convey.

The shape of the curves in Fig 13, showing an increase in oxygen, and a decrease in carbon dioxide content beyond about 19° A.T.C. is rather interesting. Presumably combustion in the precombustion chamber was nearly completed at about this point. Despite the fact that the pressure in the main combustion chamber would thereafter be decreasing somewhat more rapidly than in the precombustion chamber, it would seem that gases from the main chamber were in fact entering the precombustion chamber after 19° A.T.C., and the question arises as to whether the overall combustion in this engine is susceptible of improvement.

The authors appear to have chosen a fruitful line of attack, and the results of their further work along this line will be anticipated with keen interest.

Vote of Thanks

THE PRESIDENT: There being no further questions, I should like to propose a vote of thanks on your behalf to the authors of the paper, and I would also pay tribute to their team work in replying to the questions that have been raised.

(The vote of thanks was accorded with acclamation.)

The authors (in a written reply) said: The discussion has provided a number of suggestions and ideas for future work and several criticisms of the present work. We are extremely grateful to all the contributors for suggestions, criticisms, and general discussion of our work. We propose to reply to only a few of the many points raised.

Both Dr Barby and Mr Boddy suggest that the function of diethyl ether as a cold-starting aid is due purely to volatility (and latent heat). The experimental evidence of Cloud and Ferenezi [12] is quite clear on this point—namely, that diethyl ether has a far greater effect on the ease of cold start-

* *J. Franklin Inst.*, 1942, **17**, 143.

ing of a given fuel than does a paraffin of greater volatility, *e.g.*, *n*-pentane. Since diethyl ether has little effect on cetane rating, the mechanism by which it facilitates cold starting must differ from that by which other additives upgrade the Cetane No. of a given fuel.

Several speakers have commented upon Fig 13, which shows the analysis of combustion-chamber gases. This figure is almost identical with that given by Drinkwater and Egerton [18] (Fig 17). It is very reproducible, despite the heterogeneous conditions. The oxygen content of the gases at the sampling point drops as the flame reaches the valve. As the flame passes, the conditions become more complicated, since the concentration of oxygen and carbon dioxide behind the flame will be quite different from that in the unburnt portion of the mixture. With the geometrical position of the valve fixed, the reproducibility of these curves is excellent. They

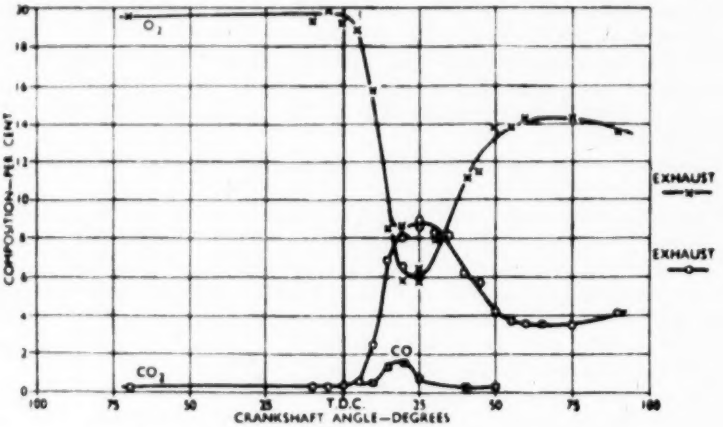

FIG 17

COMPOSITION OF COMBUSTION CHAMBER GASES[18]

were used primarily to establish the point in the stroke at which the flame arrived at the sampling point.

In the case of the peroxide and aldehyde sampling curves the majority of the samples were taken before the appearance of the flame. Our recent work has shown that variation in the geometrical position of the sampling valve in the combustion chamber has no effect upon the shape of these curves, thus showing that there are no large concentration differences in the swirl chamber during the pre-flame period.

The maker's data for the engine is 7 b.h.p. at 1200 r.p.m., giving a b.m.e.p. value of 82 for the rate of fuel consumption quoted in Table VI as against 93 calculated by Dr Barby. When using fuels of Cetane No. less than 40, rough running was experienced, the b.h.p. under these conditions being less than 7. Further data on the chemical composition of the oils used would be of little value, unless it was based upon the analysis of narrow-boiling-range fractions. For our present purposes this was unnecessary.

Mr Boddy suggests that fuel D.6 is more aromatic than the other fuels.

Aromatic hydrocarbons, such as naphthalene and its homologues, are, of course, present, but the detailed analysis of this particular gas oil shows that from 50 to 60 per cent of the carbon atoms present are in naphthenic rings. The pour point of the oil, below −40° C, is an indication of the naphthenic character of this particular oil.

The suggestion that the effect of additives both in vapour- and liquid-phase addition—and that differences in additive effectiveness on cold starting and Cetane No. are all due to purely physical effects—is not accepted. It would appear that Mr Boddy does not accept them either, since he states that " an additive must (*a*) itself be a peroxide, etc., etc."

Mr Lyn has referred to the effect of nitrogen on the Cetane No. of fuel D.6. We neglected this effect, since it is shown only by the one fuel and may well be fortuitous. The effect of benzene addition is shown by all fuels, and was repeated many times. Thus the latter effect is a general one—even though its significance is at present not understood.

Finally, we note Mr Garton's comments and agree that the effectiveness of an additive as an ignition accelerator is a function of the chemical composition of the base fuel rather than a function of the Cetane No. of the fuel.

CLASSIFICATION OF BITUMENS IN ASPHALT TECHNOLOGY BY CERTAIN RHEOLOGICAL PROPERTIES.

PART III

THE PRACTICAL VALUE OF VISCOSITY NUMBER AND RELATED INDICES AS COMPARED WITH OTHER ESTABLISHED METHODS OF BITUMEN CHARACTERIZATION

By S. L. Neppe (Fellow)

Synopsis

The criteria of a satisfactory bitumen penetration index are defined, and graphical methods based on the author's own experimental work are used to demonstrate conclusively that the indices of Pfeiffer and van Doormaal and of Holmes, Collins, and Child are basically unsound. The trends of such curves are most confusing, and contradictory conclusions may be derived from the same analytical data. According to these methods one class of bitumen may appear to be superior to another when compared for certain penetration values, whilst the reverse may apply for other degrees of hardness.

On the other hand, Viscosity Number, Softening Point Number, and Softening Point–Viscosity Number—as developed by the author in a previous publication—are shown to be fundamentally more rational in character, so that reliable conclusions may be drawn. The practical utility of these new methods of bitumen classification and their value in indicating abnormal rheological behaviour are pointed out.

Application of Indices to Experimental Data

Following the derivation of the author's new methods of bitumen classification described in Part II of this work [2] the next step was to record in the relevant tables of experimental work the respective Viscosity Numbers, Softening Point Numbers, and Softening Point–Viscosity Numbers for the numerous samples of each series of bitumens. At the same time, the corresponding penetration indices of Pfeiffer and van Doormaal [3,4] and of Holmes, Collins, and Child [5] were noted.

In order to evaluate the relative efficiency of the different methods of classification, a separate diagram has been constructed for each of the five methods in which the respective characterization indices of the numerous bitumen samples have been plotted against bitumen penetrations at 77° F (Figs 19 to 23). The points representing the members of each given series have in all cases been joined together continuously to show for each class of bitumen the trend of change in index with increase in degree of hardness.

Figs 19 and 20 show the respective penetration indices of Pfeiffer and van Doormaal (P.v.D.) and of Holmes, Collins, and Child (H.C.C.) as ordinates with " penetration at 77° F " as the abscissa in each case. Had some definite relationship existed between the P.v.D. and H.C.C. indices, it would obviously have been preferable, for the sake of direct comparison, to select the ordinate scales in such a way that equivalent indices occupied corresponding positions on the two diagrams. But reference to Figs 4

and 7 (see Part I [1]) shows that these two methods are entirely unrelated, as is evident from the comparative indices given in Table V (below) for four sets of penetration–softening point data taken at random.

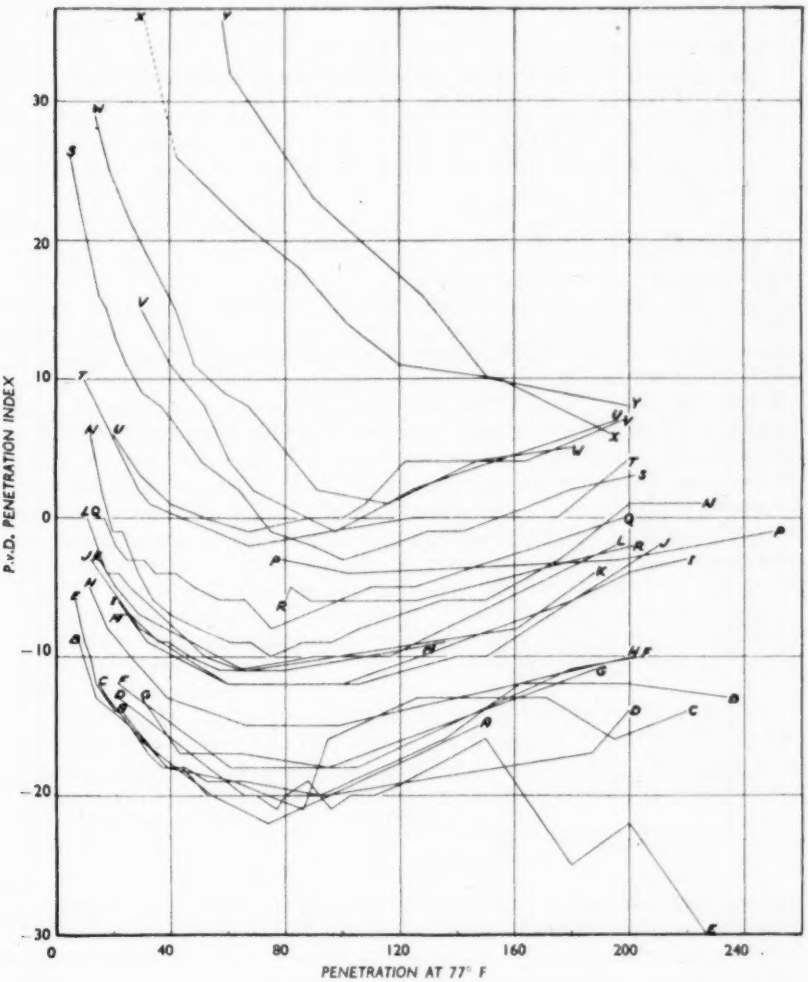

FIG 19

CHANGES IN P.V.D. PENETRATION INDEX WITH CHANGES IN PENETRATION AT 77° F

The ordinate scales of Figs 19 and 20 have accordingly been chosen only with a view to including all the available experimental data in charts of approximately similar size.

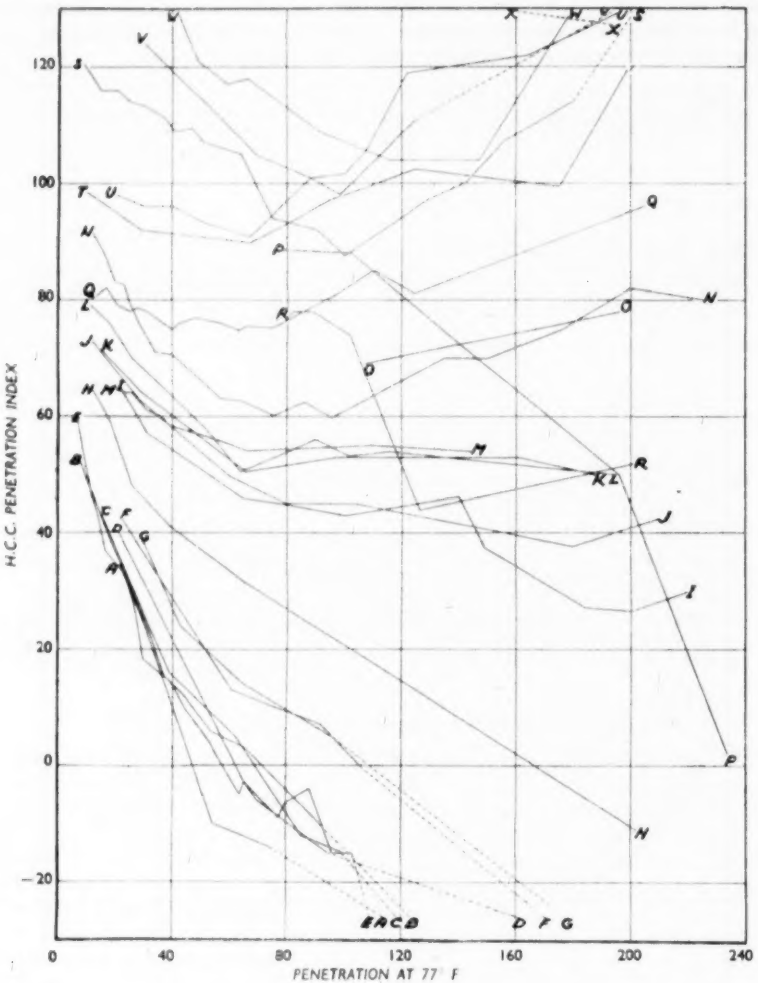

FIG 20

CHANGES IN H.C.C. PENETRATION INDEX WITH CHANGES IN PENETRATION AT 77° F

TABLE V

Comparative P.v.D. and H.C.C. Indices

Penetration at 77° F	R. & B. softening point, ° F	P.v.D. index	H.C.C. index
20	129·7	−1·9	0
200	100·0	−0·8	0
20	175·0	+2·2	+130
200	106·3	+0·5	+130

The criterion of a satisfactory penetration index includes :—

(*a*) ability to indicate " normal " materials of the same general class;

(*b*) ability to differentiate between materials of different classes; and

(*c*) ability to discern changes in internal structure arising from some physical method of hardening softer grades of parent bitumen.

How far are these requirements satisfied by the P.v.D. and H.C.C. indices as indicated by Figs 19 and 20 respectively ?

The following points emerge from a study of the two diagrams :—

1. *The P.v.D. Penetration Index Curves*

The general shape of the P.v.D. curves for any given normal series of bitumens, representing the most important portion of the penetration range from about 200 at 77° F down to 20, is more or less parabolic in shape and exhibits a minimum value. It is immediately apparent that the same class of material may have widely differing P.v.D. index values for different degrees of hardness. Thus, while it is possible to compare directly two bitumens of the same penetration at 77° F but of differing softening points (or of the same softening point but of differing penetrations at 77° F), it is extremely difficult, if not entirely impossible, to distinguish between single bitumens of different classes having dissimilar penetrations as well as softening points. In such cases it may be necessary to prepare, or obtain for each class, a series of samples representing a sufficiently wide range of penetrations at 77° F. In this event too, there can be no guarantee that the curves will not cross each other at a number of points as illustrated in many cases in Fig 19. Based on the P.v.D. Index as a standard, therefore, one class of material may appear to be superior to another when compared for certain bitumen penetrations, while the reverse may apply for other degrees of hardness.

According to Fig 19, the series of bitumens having fairly high indices (positive values) at about 200 pen at 77° F appear to be subject to far greater changes in internal structure and exhibit more complex flow characteristics on hardening than the corresponding soft samples having fairly low indices.

2. *The H.C.C. Penetration Index Curves*

Many of the remarks applicable to the P.v.D. curves also hold for the H.C.C. series depicted in Fig 20. One of the essential differences is that there appears to be no particular form of curve which aptly describes the general change in H.C.C. index with change in hardness. Series A to H are characterized by H.C.C. indices increasing rapidly from about −30 or −20 at the one end corresponding to penetrations at 77° F ranging from 100 to 200, to about +40 or +60 for penetrations lower than 20. Some of the other curves appear to be approximately parabolic as for the P.v.D. curves, but in general the trends are most confusing.

Comparative examinations of the two types of index depicted by Figs 19 and 20 respectively show that the actual order in which the various curves

occur in the two diagrams depends very largely on their shape and changes with penetration. In addition, the relative proximity of the curves in relation to each other is subject to considerable variation.

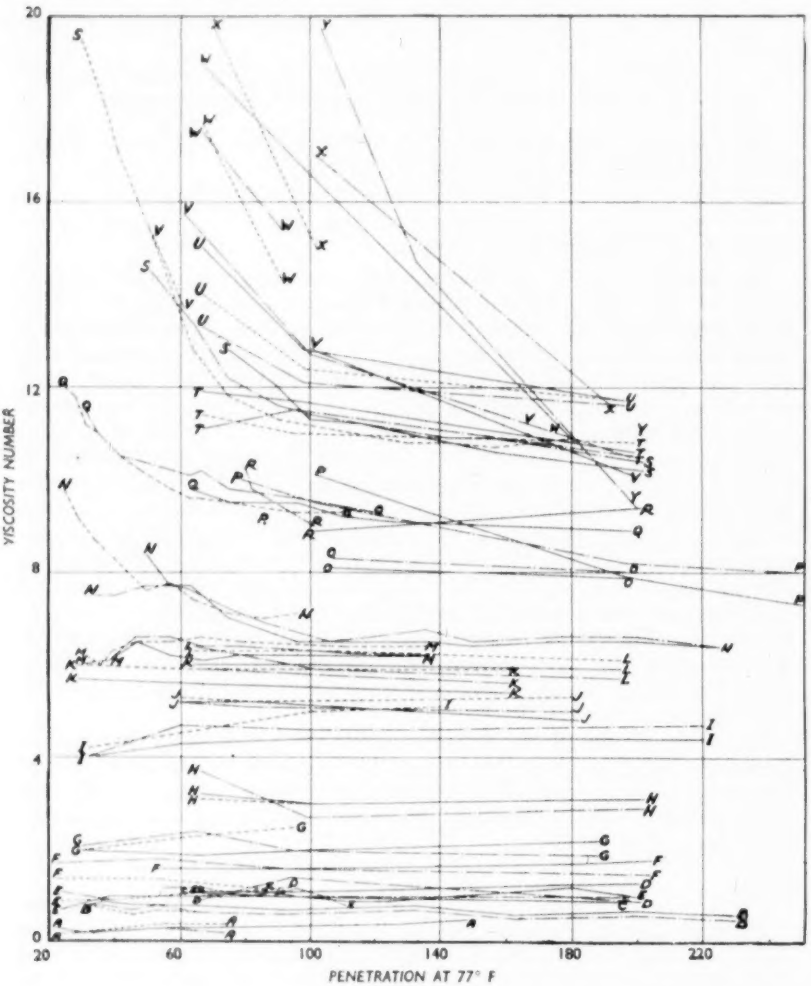

FIG 21

CHANGES IN VISCOSITY NUMBER WITH CHANGES IN PENETRATION AT 77° F

As far as changes in internal structure are concerned, Fig 20 appears to show just the opposite effect to that of Fig 19, discussed above, in that the low H.C.C. index series appear to be affected by hardening to a far greater degree than the high index series.

It is indeed disturbing that important conclusions of such a contradictory

nature should be derived from the two diagrams for the same analytical data. These findings clearly indicate the necessity for more satisfactory methods of interpreting experimental data.

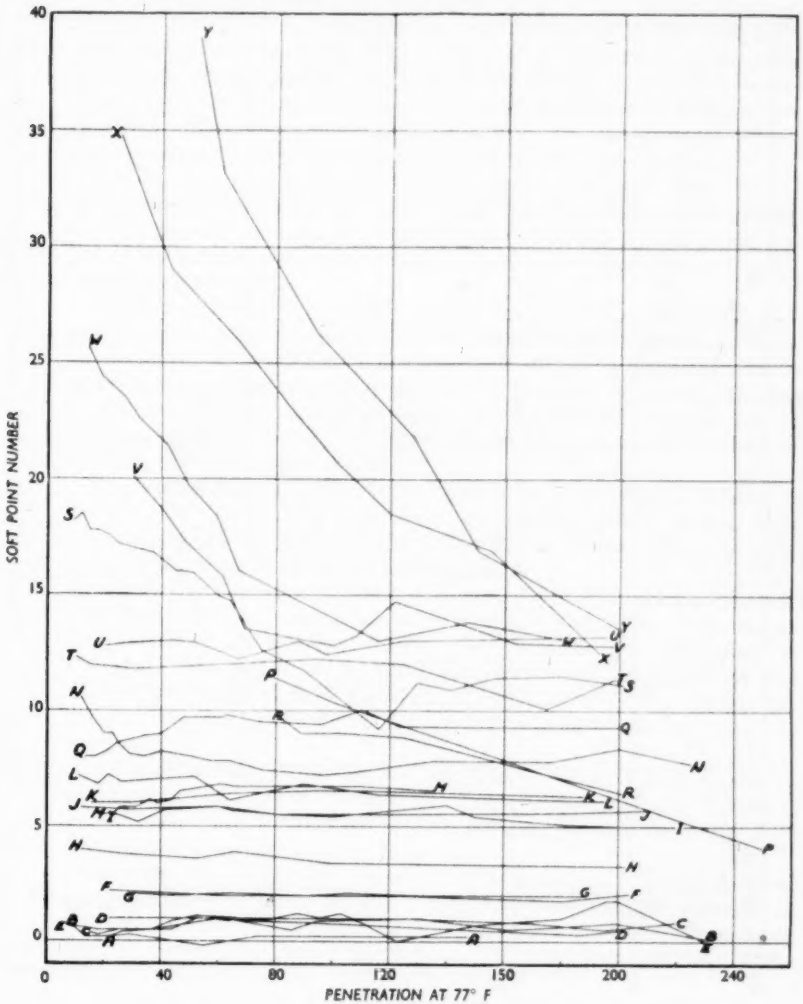

FIG 22

CHANGES IN SOFTENING POINT NUMBER WITH CHANGES IN PENETRATION AT 77° F

3. *The Curves Corresponding to the Author's Methods*

How do the indices derived by the author stand up to similar critical examination?

Fig 21 has been plotted to show changes in Viscosity Number at each of

three temperatures (viz., 140°, 150°, and 176° F) with changes in bitumen penetration at 77° F.

Fig 22 demonstrates the changes in Softening Point Number, while

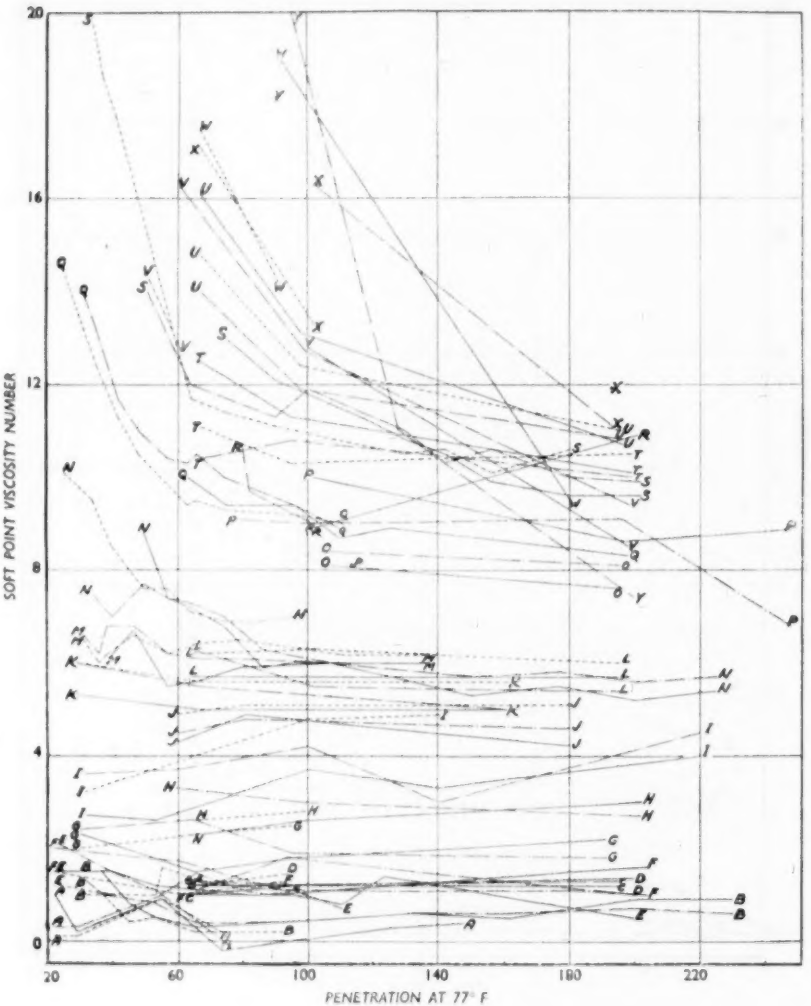

FIG 23

CHANGES IN SOFTENING POINT-VISCOSITY NUMBER WITH CHANGES IN PENETRATION AT 77° F

Fig 23, like Fig 21, gives the corresponding Softening Point–Viscosity Number curves for the same three standard temperatures.

The degree to which the three basic requirements set out earlier is satis-

fied can be seen from the following facts, which arise from a close examination of the curves in the three diagrams :—

(*a*) *Normal materials* (such as Series A to M and some others of higher indices) are immediately *characterized by the relative constancy of the indices over the whole range of bitumen penetrations.* Some small variations can be observed but these may normally be expected in this type of investigation where a considerable number of samples are handled. The discrepancies occur mainly as a consequence of certain limitations permitted by the actual experimental test methods.

(*b*) The order in which the various series occur and their relative proximity to each other in each of the diagrams under consideration are in general reasonably regular, notwithstanding that there are generally three constant temperature lines for each series in Figs 21 and 23 respectively.

(*c*) The tendency for manifestation of anomalous rheological properties, indicating changes in internal structure with increasing degree of hardness, is immediately evident from all three diagrams and in general applies to the same series of high-index samples. In this connexion, the P.v.D. indices (shown in Fig 19) are more or less in agreement, while the H.C.C. indices lead to erroneous conclusions as pointed out previously.

The actual degrees of deviation from normal rheological behaviour at 140°, 158°, and 176° F respectively can be more clearly gauged from examination of the actual index values given in the tables (not published here) than from the various diagrams.

Where the Viscosity Number, Softening Point Number, and Softening Point–Viscosity Number are reasonably identical (say within 1·0 points of the average values), the bitumens are all classed as "normal" in terms of the definition previously proposed by the author. Examination of the data shows that with few exceptions most of the samples in Series A to M, O, R, and T can be classed as normal.

Anomalous flow properties are clearly marked to a high degree in the case of the harder members of Series S, U, V, W, X, Y, and Z respectively and, to a lesser extent, are also discernible in the low-penetration samples of Series N and Q.

A point of considerable interest is that where such abnormal flow characterizes any given sample, the flow is generally less complex at 176° F than at 158° F, and again less complex at 158° F than at 140° F. This is a logical development of the general theory of the effect of temperature on viscosity properties.

A fact worth noting is that where anomalous flow is manifest in any series, the rate of increase in Viscosity Number may or may not keep pace with increase in Softening Point Number. Thus, in Series S and U, Softening Point Number lags behind Viscosity Number for the harder samples, but in Series X, Y, and Z it advances more rapidly. Such deviations are based chiefly on the relative influence of plastic and elastic properties of the bitumens at each of the three temperatures of test.

Comparative Degrees of Deviation

In order to determine the degrees of deviation of the respective characterization indices with respect to each other, four sets of diagrams (Fig 24 to 27) have been constructed in which the various indices have been plotted against Viscosity Number which, for this purpose, has been taken as the standard.

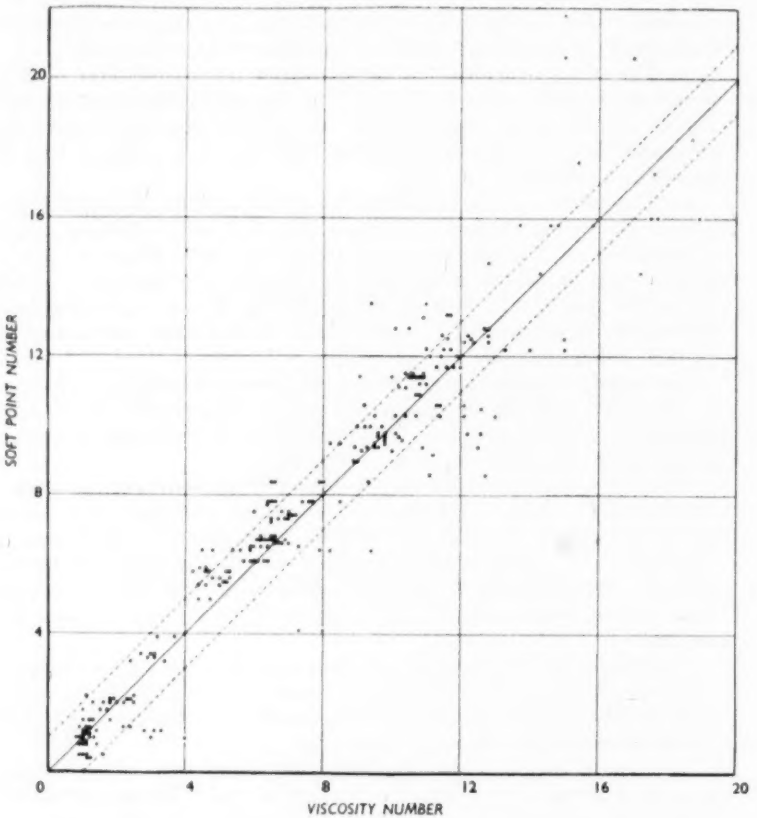

Fig 24

RELATION BETWEEN SOFTENING POINT NUMBER AND VISCOSITY NUMBER

The considerably better agreement obtained for the writer's methods of classification as compared with those of Pfeiffer and van Doormaal and of Holmes, Collins, and Child is immediately evident from Figs 24 and 25 on the one hand and from Figs 26 and 27 on the other.

Over 75 per cent of the Softening Point Numbers are within one unit of Viscosity Number and over 86 per cent within 1·5 units. In the case of Softening Point–Viscosity Numbers, the corresponding percentages are

86 and 94 respectively. The points representing the P.v.D. and H.C.C. indices respectively are, however, so scattered that it is futile to attempt inclusion in the diagrams of the best average line of proportionality.

The Irrationality of the P.v.D. and H.C.C. Penetration Indices

In order to examine the true relationship between the writer's Softening Point Number and the P.v.D. and H.C.C. penetration indices respectively,

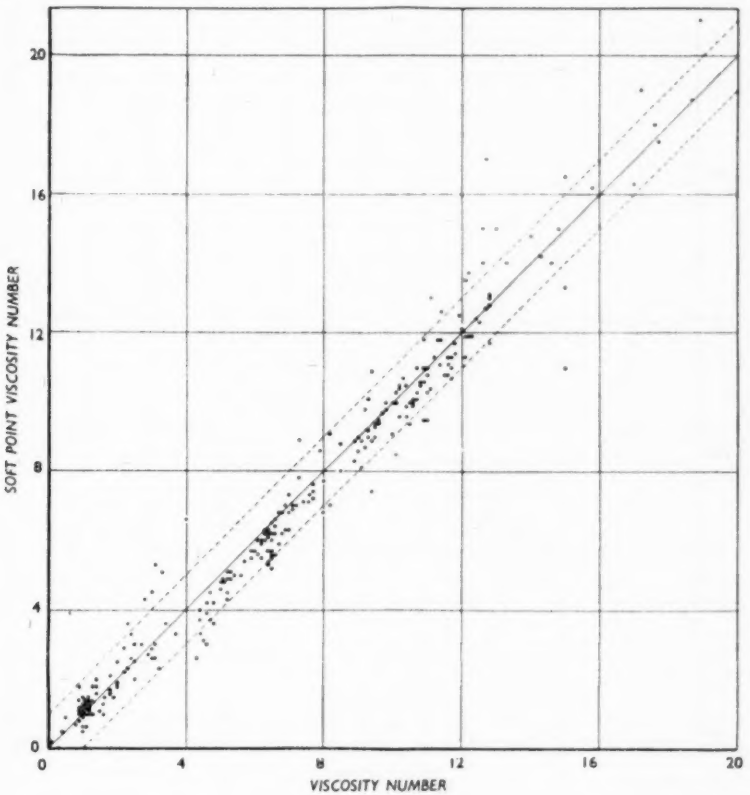

Fig 25

RELATION BETWEEN SOFTENING POINT–VISCOSITY NUMBER AND VISCOSITY NUMBER

two diagrams (Figs 28 and 29) have been constructed. In both instances the axes and scales chosen are identical and follow the procedure previously used in the construction of Figs 11 and 17 (see Part II [2]). The ordinates are thus log softening point in ° F while the abscissæ are log penetration at 77° F.

The author's lines for Softening Point Numbers of 0, 10, 20, and 30 respectively have been shown dotted in each case, and the data used for

the construction of the P.v.D. and H.C.C. penetration indices charts in Figs 4 and 7 (see part I [1]) have also been transferred to Figs 28 and 29 respectively.

From these two diagrams emerge the following interesting facts :—

(*a*) None of the other workers has made any allowance for the change in shape of the penetrometer needle below 54 penetration (see Parts I [1] and II [2]).

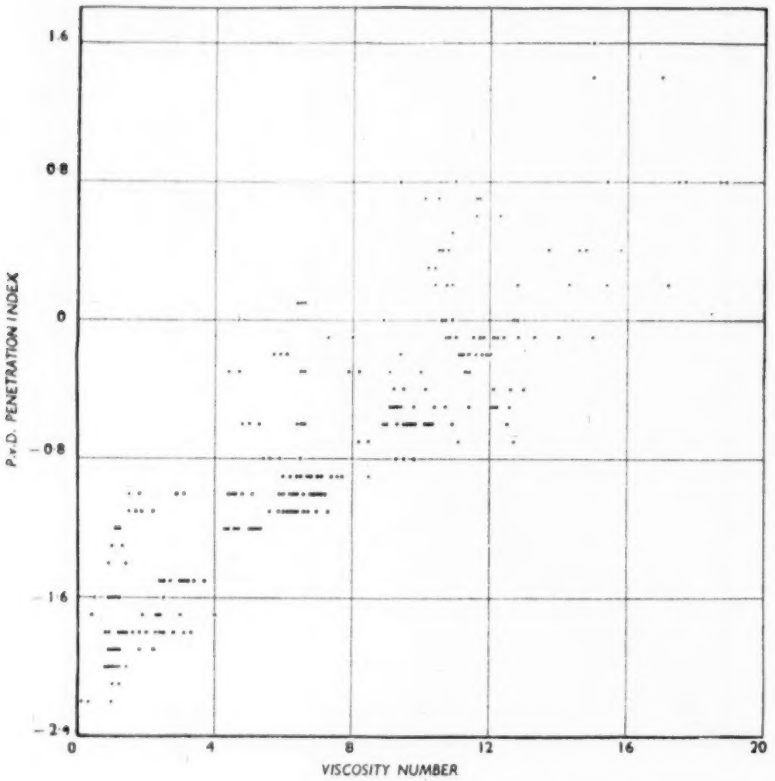

FIG 26

RELATION BETWEEN P.V.D. PENETRATION INDEX AND VISCOSITY NUMBER

(*b*) In the case of the P.v.D. indices (Fig 28), the lines assume a more and more marked convex curvature with increasing value of the index. The average slopes of the lines also increase at the same time, and in several instances follow more or less a similar trend to the author's Softening Point Number lines.

(*c*) The H.C.C. lines (Fig 29), however, are straight throughout, the slopes becoming more and more steep with increase in value of the indices. All the lines appear to originate from an extremely confined

area in the bottom right-hand corner of the chart in contrast to the findings of Pfeiffer and van Doormaal and those of the author. The H.C.C. 90 index line follows more or less the average path of the author's 10 Softening Point Number line, while the 120 index line is very close to that portion of the 20 Softening Point Number line corresponding to penetrations below 54.

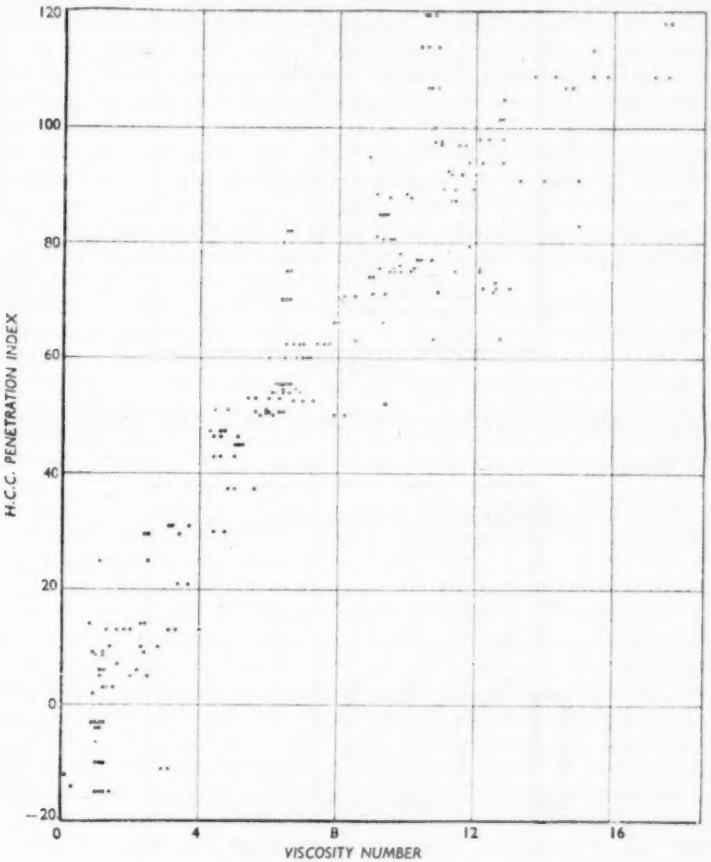

FIG 27

RELATION BETWEEN H.C.C. PENETRATION INDEX AND VISCOSITY NUMBER

Whereas the positioning and direction of the Softening Point Number lines have been derived from a close and critical study of numerous actual penetration—softening point data corresponding to "normal" bitumens from diverse sources, the foregoing discussion clearly emphasizes the extremely limited and irrational bases for the construction of the charts by Pfeiffer and van Doormaal on the one hand and by Holmes, Collins, and Child on the other.

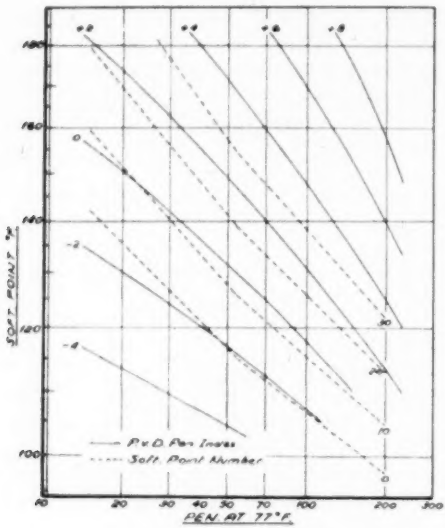

FIG 28

RELATION BETWEEN P.V.D. PENETRATION INDEX AND SOFTENING POINT NUMBER

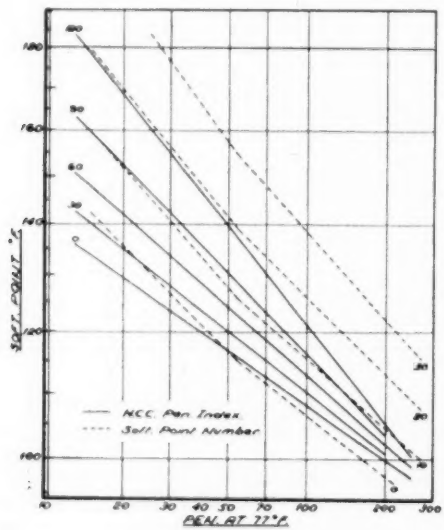

FIG 29

RELATION BETWEEN H.C.C. PENETRATION INDEX AND SOFTENING POINT NUMBER

Practical Value of the Conception Viscosity Number

Viscosity Number can assume great importance in the evaluation of crude petroleum oils as possible sources of asphaltic bitumen. Not only does this index afford a method for assessing the quality of the bitumen existing in the natural state in the crude, but it is also possible to obtain a fairly accurate picture of the probable characteristics of the combined bitumen which may result during cracking operations carried out primarily for the production of increased yields of gasoline. In such processes, the severely cracked bitumen obtained from high-temperature–high-pressure treatment of the gas oil and kerosine fractions is often blended with the straight-run bitumen. The resultant final Viscosity Number is obviously dependent on the proportion of recycle cracking stock, or intermediate distillate fractions, in relation to the natural bitumen content taken in conjunction with the viscosity characteristics of the natural bitumen itself.

Viscosity Number is also of special value for refinery control purposes in determining the proportions of different quality bitumens which may be blended to produce any desired combination.

Again, in actual plant practice, where it is desired to speed up the preparation and testing of a given class of material (*i.e.*, of known Viscosity Number), it is often more expedient to control bitumen consistency by carrying out viscosity tests at specified temperatures rather than penetrations, since accurate measurements can be made by the former method in about 30 minutes as against 2 hours for the latter. Reference to the Viscosity Number Chart immediately gives the equivalent penetration value.

It is clear, too, that direct comparisons of Viscosity Number can be made in practice between materials having entirely different penetrations and originating from diverse sources.

Viscosity Number is also extremely useful for measuring the relative susceptibility of different classes of asphaltic residuals to oxidation. Reference to the experimental data shown graphically in Fig 10 (Part II [2]) is necessary in this connexion. Thus, the relative values obtained for Series B and E respectively clearly illustrate that air blowing of the severely cracked bitumens typified by Series B has effected extremely little improvement in the Viscosity Number. A less severely cracked type, as depicted by steam-refined Series D, exhibits a slight increase in Viscosity Number on air blowing, as shown by Series H. Slightly cracked types, as indicated by Series I and M respectively, are also not very susceptible to air blowing as long as the bitumen is still soft, but display higher Viscosity Numbers as the material hardens on prolonged blowing with air (see Series K and N respectively).

With natural classes of bitumen, however, some are affected by oxidation to a far greater extent than others. Thus, Series J shows fairly consistent Viscosity Numbers on steam refining down to about 60 pen (average value 5·2), but on air blowing to the same degree of hardness (see Series L) an increase of 1·0 in Viscosity Number is obtained. Series Q and T have much in common in that, firstly, they both show gradually increasing Viscosity Numbers with hardening even by steam refining processes. Again, on air-blowing, as in Series S and U respectively, the increase in Viscosity

Number with hardening is considerably more rapid, particularly in Series S for penetrations below 50. Even more susceptible to air-blowing are the steam-refined bitumens of Series R, as indicated by Series V. Most remarkable, however, are the extremely large increases in Viscosity Number displayed by air-blown Series W, X, and Z in comparison with their equivalent steam-refined Series O, P, and Y respectively.

The exceptionally high Viscosity Numbers of Series Y and Z place these materials in a class by themselves, as the bitumen characteristics are totally unlike those of any of the other series under discussion. Even the steam-refined natural bitumens of Series Y exhibit plasticity properties to a very high degree with relatively little hardening down to 60 pen. In fact, the rate of increase of Viscosity Number with hardening is considerably more marked in steam-refined Series Y than in any of the other air-blown series which up to this stage have been considered to be particularly susceptible to oxidation. On air-blowing, the viscosity increased to such an extent that determinations, even at 176° F, for materials below 200 penetration became quite impracticable.

It is of interest to point out that this unique series of materials came to the notice of the author during a comprehensive experimental survey on the evaluation of certain crude oils as potential producers of gasoline and bitumen. The 100 pen straight-run bitumen content of the crude amounted to only 8·5 per cent by volume, but the characteristics were so remarkable as to warrant special inclusion in the present work. The material was extremely cheesy in nature, and the 300 pen bitumen contained as much as 5·4 per cent wax with a setting point of 115° F. The 300 pen sample was so unstable to heat that on vacuum distillation at a maximum temperature of as low as 525° F, considerable decomposition by cracking was evident. The solubility of the original 300 pen material prepared by steam refining was quite good both in carbon disulphide and in carbon tetrachloride, being 99·86 per cent in each case, but the 200 pen vacuum distilled sample deteriorated to such an extent that the solubility in carbon disulphide dropped to 97·85 per cent and that in carbon tetrachloride to as low as 95·63 per cent.

The conception of Viscosity Number has a great advantage over other methods of classification in that, with its aid, it is possible to ascertain whether a bitumen exhibits normal or abnormal flow characteristics under the temperature and other conditions of viscosity testing. Even comparatively small degrees of plasticity can be detected in this way.

Since the construction of the Viscosity Number chart (Fig 14, Part II [2]) is such that the vertical intercept between any two successive Viscosity Number lines in the three temperature bands is always constant, it follows that any marked numerical increase in Viscosity Number of a bitumen at a specified temperature over the average normal value for that class of material in the fluid state is in fact a direct measure of the degree of plasticity.

Whether a material has a naturally high Viscosity Number, as is the case with certain steam-refined natural bitumens, or only an apparently high index due to a large extent to a manifestation of plasticity at the temperature of testing, as in the case of some of the harder air-blown materials, can also be ascertained if additional viscosity data are obtained on the corre-

sponding softer and harder members of the same series. This point is most important, as plasticity in a material depends on a number of extraneous factors, and erroneous conclusions may be drawn unless all the information is carefully weighed. In a number of cases the author considered it advisable to prepare further members of the same series of bitumens in order to obtain additional confirmatory experimental data, particularly where the Viscosity Numbers were considerably higher at 140° F than at 158° and 176° F respectively.

It should be appreciated too that the author's method of classification is open to further expansion, and additional bands in the chart corresponding to BRTA viscosities at 122° F (50° C) and 194° F (90° C) would no doubt have great advantages in many instances, particularly where the other three specified temperatures are not quite the optimum for testing from a practical viewpoint.

In this connexion it is clear that a series of diagrams as shown in Fig 15 (Part II [2]) would be extremely valuable for ascertaining theoretically the data necessary for the construction of an extended Viscosity Number chart to include 122° and 194° F bands in addition to the existing 140°, 158°, and 176° F bands. This can be done by graphical extrapolation in either direction of the relevant straight lines representing known data for normal bitumens of log log viscosity *v* log absolute temperature for the existing three temperature bands. It would, of course, be advisable in the first place to obtain practical confirmation of the theoretical derivations.

The Viscosity Number chart has been specifically designed by the author for viscosities in BRTA seconds to suit his own work, but there is no reason why the same principle cannot also be adapted to other viscosity methods or for absolute units. It should, however, be recognized in this connexion that where anomalous flow may be displayed, different methods of test may give varying results, depending on the rates of shear used, so that when comparisons are made by different procedures, due consideration should be paid to this point. For " perfectly normal " bitumens, however, it is anticipated that greater concordancy will be obtainable irrespective of the methods of test.

It is worthy of note that in general, if Softening Point Numbers are used as the basis of evaluation instead of Viscosity Numbers as above, similar conclusions can be derived from direct comparisons of the effects of steam refining and air blowing on the same initial soft materials. Utilization of either P.v.D. or H.C.C. penetration indices, on the other hand, is far less satisfactory owing to the extreme inconsistency of the values recorded by these methods.

The unsatisfactory nature of certain specifications is not readily apparent unless some yardstick such as Softening Point Number is used. For example, the American Federal Specification calls for softening points ranging from 104° to 140° F for bitumens of 50 to 60 pen, while other States use limits of 113° to 149° F.

Lewis and Welborn [6] examined forty typical samples of 50 to 60 pen supplied by the leading producers in the U.S. and obtained softening points covering the range 118° to 137° F. The equivalent Softening Point Numbers for these samples vary from 1 to about 17, but those corresponding to the limits of the Federal specification are obviously still further

apart. With the aid of the Softening Point Number chart it is immediately evident that such specifications are of little practical value, since the limits are far too wide to allow for any clear differentiation between bitumens possessing totally different properties.

ACKNOWLEDGMENT

The author is indebted to the South African Torbanite Mining and Refining Co. Ltd. for very kind permission to utilize certain of his experimental data for purposes of this study.

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THE DETERIORATION OF TRANSFORMER OIL

PART III. ASSESSMENT AND IMPROVEMENT OF OIL STABILITY

By L. Massey *

Summary

Difficulties encountered in the operation of the nationally accepted transformer-oil oxidation test specified in BS 148 are described in detail, and the results of varying the conditions of test are shown in a series of graphs and tables. The results of an attempt to correlate the iodine values of oils with their oxidation products are given.

The need for oils of improved stability is discussed, and it is shown that uninhibited oils are giving satisfactory service in transformers operated within the design limits. On the other hand, for ventilated transformers operating under severe conditions of temperature and oxygen access or for refilling transformers in which the oil has deteriorated excessively, the use of oils of improved stability may be advantageous. The addition of oxidation inhibitors to oils appears to be the most promising form of oil improvement.

The catalytic power exerted by varying concentrations of different forms of copper has been studied, and tests are also reported which prove that some varnish films baked on copper test panels permit the migration of copper through the varnish film to oil surrounding the panel.

General

The aspects of transformer-oil deterioration of most direct importance to transformer makers and users, and which are taken into account in transformer design and maintenance, have been outlined in Parts I and II. These considerations apply generally to all transformer oils, whatever their relative merits. It is obvious, however, that oils may vary in their relative suitability and must be carefully chosen if the best performance in a transformer is to be achieved.

The engineer buys oil to the British Standard Specification No. 148 : 1951 and depends on the petroleum industry to ensure that oils meeting this specification possess the optimum combination of properties for the known conditions of service. Although most of the factors involved, such as choice of crude and methods of refining, are outside his control, he nevertheless takes an active interest, and subjects such as assessment of oxidation stability, the improvement of oxidation stability, and investigations intended to elucidate the mechanism of oil deterioration are of special interest to the transformer manufacturer's chemical staff. Part III deals with these three subjects.

Assessment of Oxidation Stability

The oxidation of an oil results in the formation of a wide range of products, and in the present state of knowledge it is impossible to estimate individually all these products, and even if this were analytically possible,

* Metropolitan–Vickers Electrical Co. Ltd.

the procedure would be far too lengthy and complicated to be suitable as a method for everyday control.

There are two methods of approach, either to use oxygen absorption as a fundamental and overall measure of stability or to oxidize and then determine the products known to be deleterious in a transformer. The former is the more exact and chemically sound method, but it does not discriminate between harmful and non-harmful products and may be an unnecessarily stringent test for an oil. The latter procedure depends on setting up empirical definitions for harmful and non-harmful products and leads to a multiplicity of tests and test conditions. Strong arguments can be made for and against every one of these empirical tests, both as regards test conditions and the suitability of the answers for correlation with service life. For the transformer manufacturer anxious to control his oil supplies there is only one course—to choose one test and acquire as much experience as possible in the operation of that test and in its correlation with per-

FIG 10

REACTION FLASK

formance of the oil in service. The preferred test for this purpose in this country for uninhibited oils is, of course, the nationally accepted oxidation test described in BS 148.

The BS 148 *Oxidation Test*

Many objections are raised to this test, but basically it appears to be a sound method of determining oxidation stability in terms of what experience shows to be the main cause of trouble in transformers, *i.e.*, sludge and acidity. It gives a result in a reasonably short time, and in addition to its main function as an acceptance test, it can, by minor changes, be adapted for research purposes. This method was evolved for uninhibited oils. It is not wholly satisfactory as a means of assessing inhibited oils, but even in this case it is capable of furnishing valuable information.

Fig 10 shows the set-up of the oxidation flask for those not familiar in detail with the method. 100 g of oil are introduced into this flask together with a piece of copper-foil catalyst. The air-inlet tube is placed centrally and reaches to within $\frac{1}{8}$ inch of the bottom of the flask. The oil is held at 150° C for 45 hr, during which period air is passed at the rate of 2 litres/hr.

At the conclusion of the oxidation period the sludge is precipitated with petroleum spirit, filtered, and weighed, and the acid value of the oil is determined. During the oxidation volatile products are returned to the flask by a water-cooled reflux condenser.

Principal objections to this test are :—

(i) That it is preferable to determine the rate of oxidation or the time necessary to reach a given degree of oxidation after a given time.

(ii) That the temperature of the test is too high and that the course of the reaction at 150° C is not the same as occurs at transformer operating temperatures.

(iii) That the test gives very poor repeatability.

The three points are inter-related. Before attempting to answer them it may be of interest to describe a number of experiments made from time to time having a bearing on the subject.

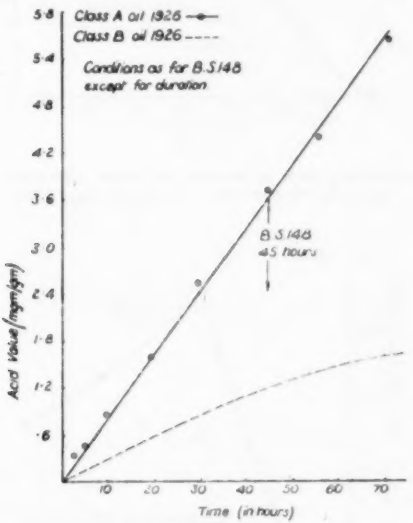

FIG 11

RELATION BETWEEN THE DURATION OF THE TEST AND THE AMOUNT OF ACIDITY PRODUCED

Variations of Conditions in the BS 148 *Oxidation Test.* The series of experimental results now to be described is taken from an investigation made by the author in 1926 on oils commercially available at that time, the object being to determine the influence of variations in the conditions of the test. These results were not published, but in spite of the lapse of time, it is believed that they are still of interest, because of their bearing not only on the manipulation technique of the test, but also on more general questions.

The oils used were of paraffinic origin, one conforming to the class A specification and the other to the class B specification. (The majority of

transformer oils of that period were derived from paraffinic crudes.) The tests gave consistent results, showing a repeatability within ±5 per cent, except for an occasional high "rogue" figure. In all the graphs shown

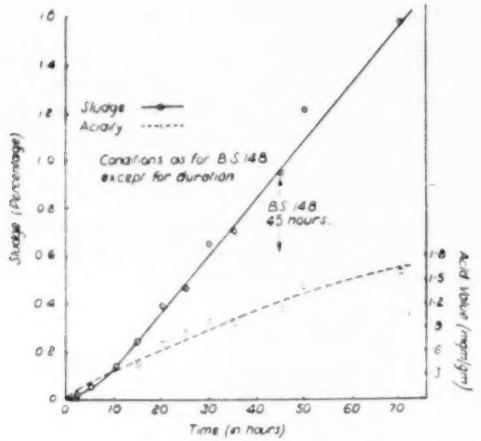

FIG 12

RELATION BETWEEN THE DURATION OF TEST AND THE AMOUNT OF SLUDGE PRODUCED. (CLASS B OIL 1926)

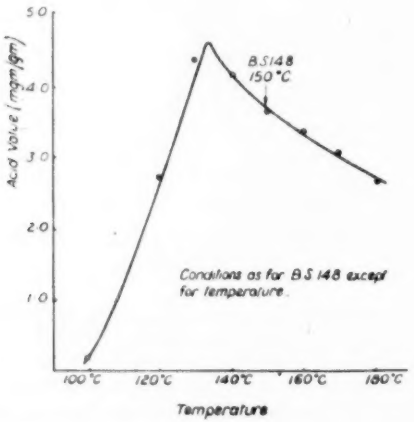

FIG 13

TEMPERATURE–ACIDITY CURVE FOR CLASS A OIL 1926

the acid-value scale has been so chosen that the curve also represents approximately the percentage of the acids present when referred to the percentage sludge scale, this being based on the assumption that the mean molecular weight of the acids is about 185.

In Figs 11 to 17 is shown the effect in the BS 148 oxidation test, of varying

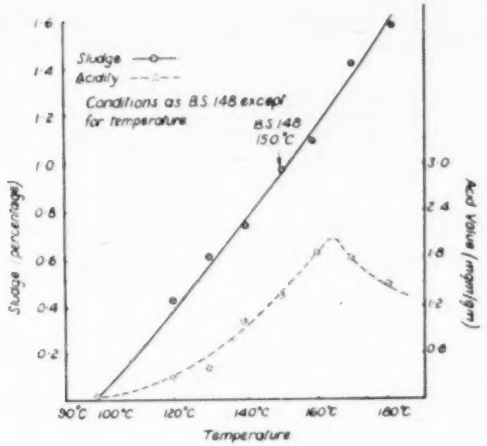

FIG 14

TEMPERATURE–SLUDGE AND TEMPERATURE–ACIDITY CURVES FOR A CLASS B OIL 1926 (FLASH POINT 165° C)

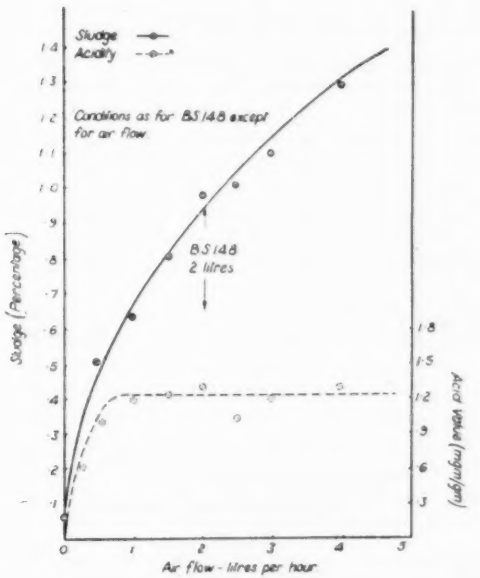

FIG 15

RELATION BETWEEN THE RATE OF THE AIR FLOW AND THE AMOUNTS OF SLUDGE AND ACIDITY PRODUCED (CLASS B OIL 1926)

the time, temperature, rate of air flow, depth of the inlet tube, and area of the catalyst. Wide variations were caused by all these factors. The influence of small variations in the internal diameter of the inlet tube was

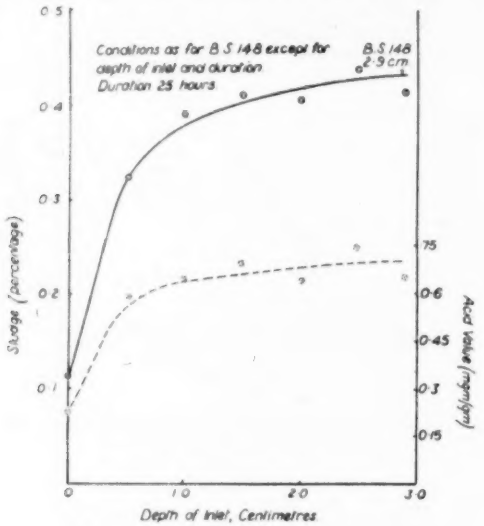

FIG 16

RELATION BETWEEN THE DEPTH OF INLET TUBE AND THE AMOUNTS OF ACIDITY AND SLUDGE PRODUCED (CLASS B OIL)

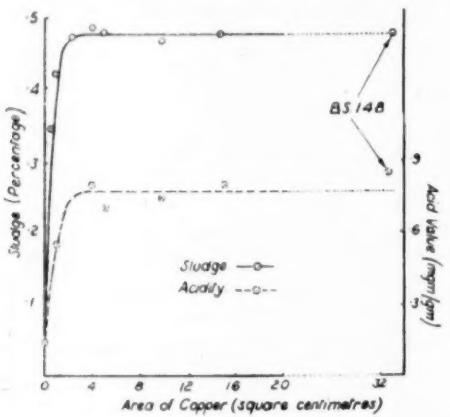

FIG 17

AREA OF CATALYST–SLUDGE AND ACIDITY (CLASS B OIL 1926) BS 148 CONDITIONS EXCEPT FOR AREA OF CATALYST AND DURATION (25 HR)

also investigated and found to be negligible (Table V). It is appreciated that the precise values of the curves shown were the characteristics of two particular oils (one class A and the other class B), but it is also believed to

be likely that the general form of the curves would apply to all oils from similar crudes. A study of these graphs will be of particular interest to

TABLE V

Influence of Variation of Bore of Air-inlet Tube

(BS 148 Oxidation Test)

Bore, mm	Sludge, %		Acidity, mg/g	
	Experimental	Average	Experimental	Average
3·0	0·47		0·70	
	0·40	0·43	0·70	0·70
	0·41		0·75	
4·0	0·42		0·80	
	0·36	0·39	0·75	0·75
4·5	0·39		0·85	
	0·39	0·41	0·80	0·75
	0·46		0·70	

those engaged in carrying out BS 148 oxidation tests, but it is only desired here to emphasize six of the more important general conclusions :—

(i) In all the tests the ratio of acid to sludge increases with decreasing intensity of oxidation conditions. The inference is that in a transformer the ratio of acid to sludge will be greater than is found in the BS 148 oxidation test.

(ii) The acidity–temperature curves show a peak which sometimes occurs below 150° C. Tests at 150° C may therefore give a misleading indication of acidities at lower temperatures.

(iii) For small areas of copper, oxidation is critically dependent on the area. The amount of exposed copper in the form of leads or straps in a transformer is likely to lie on the critical portion of the curve, but the area of the catalyst in the BS 148 oxidation test is well outside the critical range.

(iv) The sludge–time and sludge–temperature curves on the particular oils examined are approximately straight lines within the given limits.

(v) Sludge formation is critically dependent on the rate of air flow at all rates from 2 to 5 litres of air/hr. Acidity on the class B oil is critically dependent on the rate of air flow up to about $\frac{3}{4}$ litres of air per hr, but beyond this rate is independent of air flow.

(vi) Both sludge and acidity are critically dependent on the depth of the air-inlet tube at depths up to about 0·6 cm, but at greater depths they are only slightly influenced.

Repeatability of BS 148 Oxidation Test. It has been stated that the repeatability was satisfactory during the 1926 tests. This was true of most pre-war oils examined in the Company's laboratory, and in the period 1926 to 1940 it was accepted that the test method was capable of giving a repeatability of ± 5 per cent when carefully operated, with the

exception that high " rogue " figures were occasionally obtained, but as these " rogue " figures were very infrequent they were easily recognized and rejected.

During the war, however, great difficulties began to be experienced in this laboratory with an increasing scatter of results, and the rogue figures ceased to be recognizable. At one period the repeatability deteriorated to −25 per cent and +100 per cent.* A considerable amount of attention was devoted to this problem. The following series of experimental results is drawn from this investigation.

As a first step it was established that the variations occurred in the oxidation flask and not during the mechanical operation of separating the sludge from the oil. A bulk of sludged oil was taken and divided into aliquot portions, taking the greatest care to ensure that the portions were representative of the bulk. Using these portions, the influence of changes likely to occur during the performance of the specified operations by a reasonably careful laboratory technique were investigated. These included method of filtration, variations in the time the diluted oil was allowed to stand, variations in the amount of diluent, and variations in the temperature of the oil to which the diluent was added.

It was proved that, even for substantial variations in the conditions cited, consistent results were obtained. The oil used contained 0·32 per cent of sludge, and throughout the experiments the difference between maximum and minimum figures was 0·008 per cent.

Two additional experiments were made, although they covered conditions which should not occur in normal practice. In the first, 0·25 ml of water was added to the diluted oil at the time of dilution. The resultant sludge was light brown in colour, whereas the normal samples were dark brown. They were, however, identical in weight. Differences of colour in duplicate samples are often noticed when making duplicate sludge tests.

In the second experiment the oil was allowed to remain undiluted in the flask overnight, then diluted and filtered within a short time. In this case the result was 12 per cent greater than normal, which was probably due to the retentive absorption of oil by the sludge. This practice is, of course, not permitted by the specification.

The results of these experiments were to show conclusively that erratic sludge results are not due to slight changes in the mechanical processes of sludge separation. This conclusion was confirmed by determination of the acid values which followed, for a particular oil, the sludge values. Attention was therefore turned to the factors involved during the actual oxidation.

A major error was found to be caused by badly fitting ground-glass joints, which were common amongst glassware purchased during the war. It was proved that flasks with gaps in the joint of only two-thousandths of

* In making this test there is a tendency to obtain a proportion of abnormally high results, although abnormally low results are not experienced. The average of a number of test results is therefore not the half-way point between the minimum and maximum individual figures. For example, for an oil giving a mean value of 1 per cent the expression of repeatability " −25 per cent and +100 per cent " means that the individual results varied from 0·75 to 2·0 per cent sludge.

an inch gave results as high as 1·85 per cent on an oil known to have a true value of 0·85 per cent. It was also found that joints sound at the start of the test were leaking at the conclusion and that difficulties in opening the flasks after the tests sometimes induced operators not to screw home the joints firmly in the first instance. When these matters were put right the bigger errors disappeared, but on the particular wartime oil used, notwithstanding the greatest care, the repeatability could not be improved beyond −25 per cent and +40 per cent. These limits also held for other transformer oils current at the time. On the other hand, the same operators, at the same time and using the same equipment, consistently obtained without difficulty a repeatability well within ±5 per cent on non-inhibited turbine oils of approximately 1 per cent sludge, in spite of the fact that some of the glassware must have had badly fitting joints. It therefore seemed certain that the scatter of acidity and sludge results on transformer oil was influenced by some unknown characteristic of the oil and not only by faulty manipulation of the method.

Apart from the strictly practical value of the findings, it is extremely interesting to know that such a small gap as 0·002, which should have been self-sealing with condensed oil, could affect the oxidation to such a great extent. In following up this finding a transformer oil was sludged in a flask under the normal conditions except that the condenser was removed. The result was a series of figures ranging from 1·2 to 2·2 per cent (Oil A1, Table VI). When the test was repeated a number of times the same high and variable figures resulted.

TABLE VI

Open-flask Oxidation Tests

(Sludge results obtained by BS 148 oxidation test modified by omitting reflux condensers)

	Oil A1	Oil A2
% Sludge (mean of large No. of determinations by standard method)	0·85	0·82
% Sludge with reflux condenser removed (individual results)	2·14 2·17 1·56 2·20 1·56 1·52 1·54 1·51 1·62 1·57 1·94 1·28	0·66 0·76 0·67 0·77 0·68 0·86 0·64 0·78 0·63 0·77 0·57 0·77

In the post-war period a transformer oil was selected which yielded rather more consistent sludge results (−12 per cent and +17 per cent), and on this the open-flask tests were made. The results were fairly consistent, being slightly lower, not higher, than the sludge by the standard test (Oil A2, Table VI).

These results established a very definite difference between the two transformer oils (*i.e.*, the wartime oil and the post-war oil). In the wartime oil (A1) the result of the oxidation was critically dependent on the atmospheric conditions above the oil (*i.e.*, in the air space of the flask and the reflux condenser), whereas on the post-war oil (A2) they were not.

These results suggested a possible explanation of the anomaly that

difficulties in repeatability were not experienced with turbine oils, *i.e.*, the turbine oil was still less susceptible to the air-space and reflux conditions.

It was thought that some light might be thrown on the problem by carrying out oxidation tests with the air inlet arranged not to dip into the oil but to deliver air above the oil surface. A test was made on a turbine oil and on the wartime oil with the tube orifices ¼ inch above the oil surface. A corresponding figure was available on the 1926 class B oil. The results are given in Table VII. It will be seen that the ratio of the results by the

TABLE VII

Tests with Air Inlet ¼ inch above Oil Level

(Modified BS 148 oxidation test)

Oil	Flash point (closed), ° C	Sludge, %	
		Standard method (mean value)	Inlet above oil (individual values)
Wartime transformer oil .	148	0·85	0·16, 0·10, 0·17
1926 transformer oil . .	165	0·95	0·11 (mean of 6)
1946 turbine oil . . .	195	1·03	0·035, 0·017

normal method to those obtained by the method with the air inlet above the oil is very much greater for the turbine oil than for the transformer oils, *i.e.*, the turbine oil is very little oxidized by the passage of air across the surface, but the transformer oils are appreciably oxidized.

The influence exerted by the vapour space above the oil and by oxidation at the surface of the oil was also illustrated by an experiment in which the flask was filled to the neck with 180 g of transformer oil (A1) and then sludged by the normal method. In spite of the greater bulk of oil the result was the formation of only 0·4 g of sludge as against the normal of about 0·85 g (*i.e.*, 0·22 per cent on the 180 g against 0·85 per cent on 100 g).

The experiments generally confirmed that whereas on some oils the sludge and acidity results are dependent on the conditions in the air space above the oil (*i.e.*, in the flask and condenser), on other oils they are not, the latter type yielding the more consistent results.

This lends some experimental support to the previously unsubstantiated opinion held in this laboratory that some oils are inherently liable to give inconsistent results.

It may be pointed out that the difference in behaviour found in the open flask and associated experiments is in agreement with the work of Gossling and Romney,[1] who proved that the sludge and acidity values of some oils are influenced by the temperature of the reflux water, increase in reflux temperature resulting in increase in sludge and acidity.

At one time the author had linked this apparent dependence of the sludge and acidity on the air-space conditions with the fact, shown by examination of routine control records, that the tendency to erratic results coincided with a decrease in flash points. Pre-war oils frequently had closed flash points of 165° C as against the 145° C of the wartime oils, and it was suggested that it was undesirable to oxidize an oil at a temperature

above its flash point under which condition a very high vapour pressure could be expected. Numerous experiments, however, proved the incorrectness of this theory. In particular, both the wartime and the post-war oils referred to had low flash points (145° C and 152° C respectively), and the loss in weight of the oil during the open flask experiments was 30 per cent in both cases. (The loss in weight of these oils under the conditions of the standard BS 148 oxidation was about 1 per cent.

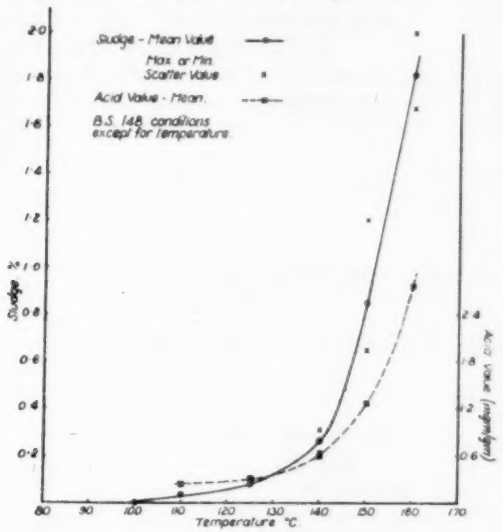

FIG 18

TEMPERATURE–SLUDGE CURVE ON WARTIME OIL A1 (FLASH POINT 145° C)

In another test a transformer oil of 0·85 per cent sludge was distilled under vacuum in a current of nitrogen in order to provide residual oils of higher flash points. The results are given in Table VIII. There is negligible

TABLE VIII

Sludge Tests on Fractionally Distilled Transformer Oil

Fraction	Sludge, %	Acid value, mg/g
(*a*) Residue of flashpoint 156° C . .	0·64 0·74	0·9 0·9
(*b*) ,, ,, 164° C . .	0·80 0·78	1·3 1·0
(*c*) ,, ,, 166° C . .	0·83 0·78	1·2 1·1
(*d*) ,, ,, 176° C . .	0·80 0·80	0·9 1·1
Distillate from (*d*)	0·80 0·83	1·8 1·7
Original oil, 145° C	0·85 (mean)	1·3 (mean)

difference in the sludge results in the various fractions, although the acid value of the distillate is rather higher than the acid values of the residual oils.

While engaged on this work on repeatability, it was thought that sludge–temperature curves might throw some light on the problem, and four

typical wartime and post-war oils were examined. The results are shown in Figs 18 to 21. Throughout this work the repeatability was poor, and the precise form of the curves is therefore influenced by a chance factor, but

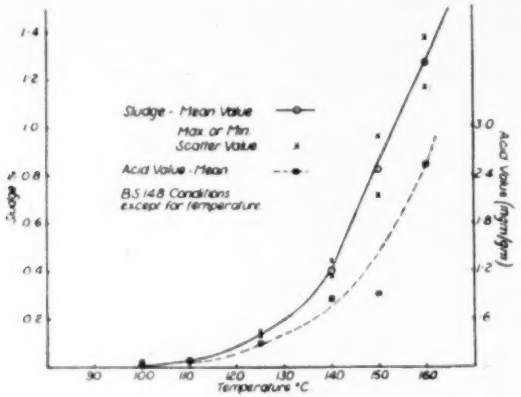

FIG 19

TEMPERATURE–SLUDGE CURVE ON POST-WAR OIL B (FLASH POINT 152° C)

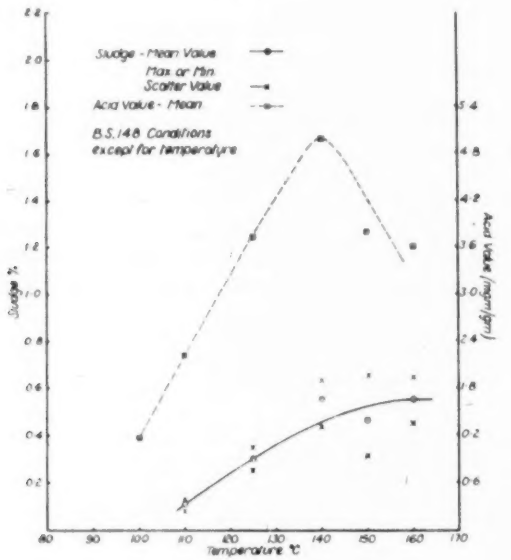

FIG 20

TEMPERATURE–SLUDGE CURVE ON POST-WAR OIL C (FLASH POINT 154° C)

the mean values at each temperature were based on a reasonable number of results—as many as fifteen in some cases. Scatter limits are shown as well as mean values.

Oil A1 was the wartime oil quoted earlier as causing so much repeatability trouble, oils B and D were typical post-war low-acid-forming oils, oil C was a post-war high-acid-forming oil.

It is only desired to draw attention to three points from these curves :—

(i) All the oils (Figs 18 to 21) show a marked change in the sludge–temperature slope between 120° and 150° C and in this respect differ from the 1926 oil (Fig 14), which gave a linear relationship between these temperatures. This may be associated with the change from paraffinic to naphthenic crudes.

(ii) The scatter of results tends to increase with rise in temperature.

(iii) The high-acid-forming oil exhibited a marked acid-value peak below 150° C, resembling in this respect the 1926 class A oil.

Conclusions concerning the BS 148 *Test.* With the assistance of some of the data presented above and of other published data, some comments can

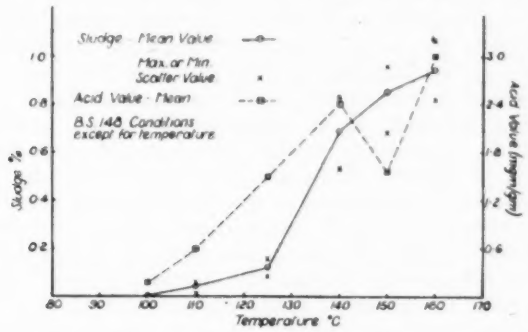

FIG 21

TEMPERATURE–SLUDGE CURVE ON POST-WAR OIL D (FLASH POINT 144° C)

now be made on the three objections raised to the BS 148 test which were : that the answer should be in terms of the rate of oxidation or the time to reach a given point of oxidation, that the temperature is too high, and that the repeatability is very poor.

As regards the first point, the only time-oxidation products curves determined on the oils discussed in this paper are those given in Figs 9 and 14. No very great error would be involved in treating these as straight lines. They exhibit change of slope chiefly in the initial period, this being partly a characteristic of the oil and partly of the catalyst used. These statements are also true of a number of other oils examined in this laboratory, but unfortunately detailed records are not available. For oils of this type, the fixed time test is equally as satisfactory as the fixed oxidation-products-limit test or the rate-of-oxidation test.

There is published evidence, however, that many oils, when tested by other oxidation methods, change rapidly in rate of oxidation with time. For example, Ham and Thompson report widely different forms of time–oxygen-absorption curves for different oils,[2] and it is possible that these oils would yield widely differing shapes of curves if tested by the BS 148

oxidation test method. This is an undesirable disadvantage of the fixed-time method, for it is of obvious value to know both the length of the induction period and the oxidation rates after this period. The relative merits of oils can be completely assessed only when the sludge–time and acidity–time characteristics are completely explored.

On the other hand, it has never been claimed that the BS 148 oxidation test is suitable for rating oils according to small differences in order of merit —it aims only at discriminating between suitable and unsuitable oils. That it has achieved this object is proved by experience over many years. Oils meeting the sludge limit of the 1933 edition of this specification have proved free from any serious sludge-forming troubles in service, whereas sludging troubles were common in transformers in the period before the national acceptance of this specification. The defect of this earlier specification was that it did not set an acidity limit as well as a sludge limit. Considerable experience, however, is also available on this point. Class B oils developing during the oxidation test an acid value of not more than 1·5 have given trouble-free performance over many years, whereas class A oils developing an acid value of about 4·5 and class B oils of acid values above 3·5 have given acidity and corrosion troubles in service. This defect has been remedied in the 1951 edition of the specification.

Finally, it is far easier in an industrial laboratory handling a large volume of work to make one determination after a given period rather than a number of determinations lasting an indefinite period.

On the question of temperature of the test, the whole trend of the data shown is to indicate that at all temperatures up to 120° C the oxidation behaviour of the oils examined is regularly progressive, but that above this temperature the behaviour changes and becomes erratic : the oxidation rate may increase, the scatter of results increases, peaks occur in the acid-value curves, and, in general, the oil becomes unstable and the oxidation is influenced by very small uncontrollable factors.

It has previously been stated that the maximum permissible copper temperature in a normally operated transformer is 115° C. On first consideration therefore it would appear that a test temperature in this region, *e.g.*, 120° C, would be far preferable to 150° C.

There are two difficulties, however, in the way of this change. First, the amounts of sludge and acidity formed in a reasonable test period would be too small to be an index of degree of oxidation, and secondly, the test would not cover the behaviour of those films of oil raised to much higher temperatures during short-circuit conditions. The first objection may be capable of solution by examining other criteria of oxidation resistance—for example, interfacial tension and peroxide values. The second objection calls for an investigation into the possible magnitude of catalytic influences on the main oil bulk exerted by very small volumes of oil raised to high temperatures for very short periods in contact with copper.

Until these questions are settled the present test temperature of 150° C appears to be a reasonable figure.

It seems a pity, however, that the method of refining an oil and the maintenance of the sludge-test temperature at a value which is chemically too high should be governed partly by the need to cater for a risk (which may never materialize in many transformers) of a short-circuit condition

raising a thin layer of oil to a high temperature for a very short period, unless it is proved that these thin layers catalyse the main bulk of the oil.

The third criticism is poor repeatability. If the evidence is accepted that some oils are unstable and erratic in the sludge test, then the answer is clear—unstable oils are unsuitable for use in transformers. If an oil gives erratic results due to minor changes in the atmosphere above it and in the refluxing conditions, then these factors may also operate in a ventilated transformer. An oil giving double the sludge in an open flask as compared with the refluxed flask is obviously more open to suspicion than an oil which gives the same result under the two conditions, and this behaviour may prove to be a fair reason for rejection.

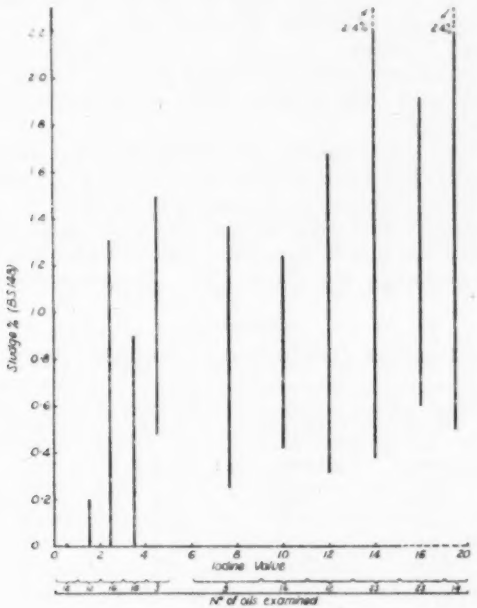

FIG 22

SLUDGE–IODINE VALUE (WIJS)

Thick lines indicate range of sludge values on oils grouped according to their iodine value

From the foregoing considerations it appears to be justifiable to suggest that in its present form the BS 148 oxidation test is performing a useful service and has gained the confidence of the oil user. In the present state of knowledge it would be undesirable to modify its conditions. It may in the future be found necessary to modify or even supplant it by one of the other methods which have been proposed, but such a step must wait on a greater degree of agreement than has yet been reached, and on the collection of evidence correlating the laboratory test results of these alternative methods with service performance of the oil.

Iodine Value as a Measure of Oxidation Stability

Before concluding the section of this paper dealing with laboratory measures of oxidation stability, it may be of interest to mention some work carried out in an attempt to correlate iodine values and oxidation characteristics of oils.

In the early stages of transformer-oil development it was customary to determine the Wijs iodine value (IP 84/45T) as a matter of routine. Analysis in 1926 of the records of this laboratory yielded the figures summarized in Fig 22. The degree of correlation between iodine value and amount of sludge proved very disappointing, but it is interesting to note two points. Every oil of iodine value less than 1 gave negligible sludge, every oil of iodine value greater than 5 yielded appreciable sludge. This held true for every one of the 152 oils examined.

After this first attempt at correlation it was decided that there might possibly be stronger evidence of a relation between iodine value and total products of oxidation than between iodine value and one particular class of oxidation product.

Insufficient data were available concerning all the products of oxidation to test this theory, but a better figure than sludge alone would be the sum of the amounts of sludge and acids present in the oil.

Oils of increasing iodine value were sought and a table prepared of their iodine values and the sum of the percentages of sludge and acids obtained in the BS 148 oxidation test (Table IX). The percentages of acids were

TABLE IX

Correlation of Iodine Value and Oxidation Products

Date of supply	Iodine value (WIJS)	Sludge BS 148	Acid value, mg/g	Acids, % approx	Sludge, % + Acids %
1926	0·1	0·05	5·4	1·80	1·8
	0·4	0·04	3·7	1·23	1·3
	0·5	0·03	3·4	1·13	1·2
	1·17	0·12	3·1	1·03	1·1
	9·6	0·90	1·8	0·60	1·5
	14·3	0·99	1·8	0·60	1·6
	16·7	0·96	1·2	0·40	1·4
	21·0	1·25	1·1	0·37	1·6
1949	3·2	0·79	1·5	0·5	1·3
	6·4	0·52	3·5	1·17	1·7
	6·7	0·82	0·9	0·3	1·1
1947	7·1	0·85	1·3	0·43	1·3

calculated from the acid values of the oils, taking the mean molecular weights (M.M.W.) of the acids as 185. (This figure was determined by separating the acids from the oil, determining their saponification value, and calculating the M.M.W. on the assumption that the acids were monobasic. The acids from all the oils of the 1926 series approximated to this figure of 185.) The figures given in Table IX are for individual oils, *i.e.*, they are not the averages for groups of oils. The oils in the top portion of the table were typical oils current in 1926, and were probably all from

paraffinic crudes. The decrease in acidity with rise in iodine value will be well known, but the point of great interest is that in every case, in spite of the differing degrees of refinement, the sum of the amounts of acids and sludge lies between the limits of 1·1 and 1·9 per cent. In the lower part of the table is given the result of corresponding tests on several post-war transformer oils. The iodine values and acid values do not fit so exactly into the relationship shown by the earlier oils, but this was to be expected, as these oils were from totally different crudes. It is very remarkable, however, in view of the difference in crudes and the other changes which must have occurred during the long periods elapsing between the two sets of samples, that the values for the amounts of sludge plus acids still lie between 1·1 and 1·9 per cent. (It must be pointed out that all the results quoted in this paper are on oils in the " finished " state as supplied to transformer users, none relating to oils in earlier stages of refinement.)

The inference is obvious. If, in producing an oil to meet the standard British specification, changes in the nature of the crude and methods of refinement produce only small changes in the total of the oxidation products, then the choice of an oil can depend only on selecting one in which as few of the products as possible are harmful. In practice it means the specification of compromise values for acids and sludge. This step is taken in the latest British Standard (BS 148 : 1951), although some transformer manufacturers have been pursuing this course for some years.

Improvement of Oil Stability

Need for Oils of Improved Oxidation Stability

Before dealing with methods of improving the oxidation stability of an oil, it is perhaps desirable to consider what need exists for improved oils.

It is generally accepted that oils complying with BS 148 : 1951 are perfectly satisfactory when used in transformers operated within the designers' limits and with reasonable maintenance attention. This satisfactory state of affairs applies to all conservator transformers and to the majority of ventilated-type transformers. Under such conditions an oil life of twenty years is common, and there is need for oils of improved stability.

In the class of ventilated transformers, however, there occurs a small percentage of cases in which the oil stability is unsatisfactory. These cases may not be due entirely to the oil but to excessive loading or to other features of construction which increase the oxidation rate of the oil. Users of oil who have experienced these troubles are emphatically of the opinion that oils of improved stability should be available even though these occurrences are rare.

At the present time the operating temperatures of transformers are based on the performance of the solid insulants rather than on the limitations of the oil. Improvements in solid insulants may enable transformers to be designed for operation at higher temperatures, thereby increasing efficiency, and this will in turn create a demand for oils of improved stability at higher temperatures than are now necessary.

In connexion with this temperature factor it may well be that some of the long oil lives experienced are possible because of the fact that so many transformers have in the past been operated well within their maximum

load rating and consequently at comparatively low temperatures, say 50° to 60° C. During the war, however, shortage of equipment caused increased loading, and in some cases operating temperatures began to rise to the permitted maximum of 85° C. For reasons of efficiency and economy, and because of the continuing national shortage of generating plant, this trend may continue. Applying the 10° C rule (*i.e.*, that oxidation rate is doubled for every rise of 10° C) an oil having a life of twenty years at 60° C may only have a life of five years at 80° C.

Another point is that, although all oils in correctly maintained transformers give satisfactory performance, any deviation from normal conditions is frequently followed by oil trouble. This is general evidence that there is no great factor of safety in the oils' characteristics and that any increase in the severity of operating conditions cannot be catered for by the present uninhibited oils.

From the foregoing considerations it would appear that there is a need for two classes of oil. Oils complying with the provisions of BS 148 : 1951 meet the requirements for all conservator transformers and for ventilated transformers not operating under severe conditions of service. In these cases there is no need for oils of improved stability.

Oils of improved stability are needed for ventilated transformers operating under severe conditions of loading and for transformers in which features of design are responsible for increasing the severity of the conditions promoting oxidation. They can also be used with advantage for refilling transformers in which excessive oil deterioration has occurred, for apart from the risk that the severe conditions may persist after refilling, there will be less risk of the new oil deteriorating rapidly as a result of the presence of traces of the old oil. Oils of improved stability will also, no doubt, be required in the future, in consequence of the trend towards increased electrical efficiencies and increased operating temperatures.

Methods of Improving Oil Stability

Most petroleum technologists believe that no great improvement in the oxidation stability of transformer oils can be expected from improvements in the present methods of refinement, which have attained a high degree of efficiency.

In general, an oil refined to produce on oxidation only small amounts of sludge will produce comparatively high amounts of acidity, and vice versa. Some degree of improvement in the sum of these two products of oxidation is presumably possible by choice of crude, but oil suppliers are no doubt limited in this respect by world conditions, and oils meeting the oxidation test of the 1951 revision of BS 148 are likely to be the best that can be produced by refining processes.

A very great improvement in oxidation stability can, however, be achieved by the addition of small quantities of anti-oxidants to an oil, and future developments are likely to be in this field.

Transformer-oil history can be divided into three phases. First, the period of high-sludge oils during which acidity troubles were negligible but sludge troubles prominent. This led to the use of the sludge value as a

sole criterion of an oil and the consequent development of highly refined low-sludge-forming class A oils. Secondly, the period of class A oils during which acidity troubles were experienced in transformers. Thirdly, the present period of class B oils selected on compromise values of sludge and acidity, and during which very little trouble is being experienced with normally loaded transformers.

It seems possible that a fourth phase, that of oxidation-inhibited transformer oils, has now commenced.

Inhibited Oils

Although the chemical and laboratory development of transformer oils inhibited against oxidation is now far advanced, the practical development has lagged very greatly behind that of the inhibited turbine oils, which are now well established in engineering practice. This may partly be due to the difference in the conditions of service. In a turbine these conditions are well defined and the oil comes into contact only with water and metals, so that performance in service can fairly safely be predicted on the results of laboratory tests. In a transformer conditions are more complex, particularly because there are so many organic insulating materials present, with a resultant risk of specific reactions between particular insulants and particular inhibitors. The general approach in the United Kingdom has been to argue that if an inhibitor is added to a base oil which itself passes BS 148, then the failure of the inhibitor would not cause a situation worse than would be the case if the uninhibited oil had been used in the first place. Until more experience in the field is available this cautious policy appears to be justified, although the petroleum technologist is not satisfied that oils complying with BS 148 are the most responsive to additions of inhibitors.

There is a considerable volume of published information favourable to the use of inhibited oils, but one or two adverse comments have appeared. For example, Treanor and Raab [3] report some field tests and, among other adverse comments on inhibited oil, they state that one oil showed a runaway development of sludge and acidity after the inhibitor had been used up, the oxidation rate then being much greater than that for the uninhibited base oil. This is a particularly unfortunate statement in view of the accepted British policy. It should be pointed out that the user of oil is inclined to attach more importance to the evidence supporting one unfavourable opinion than to that supporting many favourable opinions. This cautious attitude is, of course, justifiable. If a chemical manufacturer or oil supplier turns out a faulty batch of material, the only financial loss to him is the cost of that batch. If a faulty material is put into expensive electrical equipment it may endanger that equipment, which costs a sum of money quite disproportionate to the cost of the faulty material.

The runaway characteristics reported by Treanor and Raab may well have been associated with an unsuitable matching of oil and inhibitor. It is, for example, suspected that two commercially available oils examined some time ago in this laboratory were deficient in this respect. These oils, together with their base oils, were subjected to the BS 148 oxidation test, and in one case the inhibited oil yielded sludge and acidity results

slightly greater than those on the base oil, and in the second case the sludge and acidity were only slightly less than the results on the base oil. Whilst the BS test is not suitable for complete assessment of an inhibited oil, it is the author's opinion that an inhibited oil must at least show negligible sludge and acidity when tested by this method.

Alternatively to the suggestion that the inhibited oils referred to above yielded poor results because of poor matching of oil and inhibitor, it is not impossible that the poor results of the BS 148 test were due to the use of an inhibitor unstable at 150° C. The view has in the past been expressed by some oil suppliers that as the operating temperatures of transformers do not exceed 85° C, there is no need for the inhibitor to be stable above this temperature. This is not so, for the success of inhibited oils will depend partly on their ability to minimize oxidation at the higher temperatures. Recent samples of inhibited oil have all met the requirement that negligible sludge and acidity must be formed during the BS 148 oxidation test, and in general, the mistakes experienced during the early history of inhibited oils in the United Kingdom have been corrected. There is also a growing volume of satisfactory field experience.

If the views advanced concerning the functions of inhibited and uninhibited oils are accepted it seems logical to suggest that inhibited oils should be tested at 150° C and uninhibited oils at 120° C, providing, of course, that suitable criteria of the degree of oxidation can be found in the latter case.

Catalysis of Oil Oxidation by Copper and its Compounds

The importance of copper in the study of transformer-oil oxidation behaviour has been emphasized by many of the data so far presented in this paper. It is an essential—and probably the most active—material of construction of a transformer, and it is the catalyst most commonly used in accelerated laboratory oxidation tests. In this section are recorded the results of some experiments exploring the behaviour of copper and its compounds under varying conditions and in varying concentrations. In most cases the experiments have been made employing modifications of the BS 148 oxidation test method. No attempt is made to suggest theories for the mechanisms involved, but it is hoped that the data given will be of some value to those interested in this field.

Metallic Copper in Presence of Oil Acids

In some of the experiments so far described copper has been shown to be more active in acid oil than in neutral oil. In the 1926 series of tests a time–sludge plot was determined by the BS 148 oxidation method on new oil to which had been added sufficient acid oil to bring the acid value of the mixture to 0·2 mg/g. (The acid oil was prepared by oxidizing the same original oil in a BS 148 oxidation flask and filtering off all insoluble matter.) The results are given in Fig 23, where they are compared with the results on the original neutral oil. It will be seen that the low concentration of acidity increases the initial rate of sludge formation and eliminates the small induction period observable in the neutral oil. For longer periods, however, the curves tend to coincide and the results lie

within the experimental error of the test. The tests were repeated on an oil adjusted to an acid value of 0·5 mg/g, and identical results were obtained.

From the practical point of view it may be inferred that the use of an acid oil in the original fill-up of a transformer would result in more rapid deterioration in its early history than would occur with a neutral oil. This emphasizes the importance of varnish acids which probably behave in a similar manner.

Soluble Copper

The use of oil-soluble copper compounds as catalysts in oil-oxidation tests has received attention for many years, and the presence of soluble copper in transformer oil in service is possible as a result of interaction between metallic copper and varnish acids.

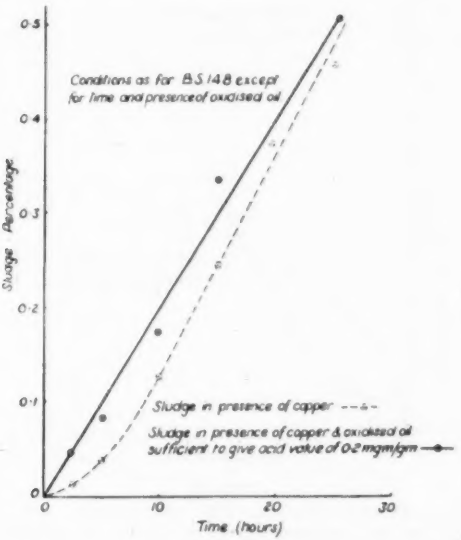

FIG 23

THE CATALYTIC EFFECT OF THE ACIDS PRESENT IN OXIDIZED OIL (CLASS B OIL 1926)

Some attention was given to soluble copper in the 1926 series of tests, and one curve of particular interest was obtained. A paraffinic oil containing 0·05 per cent of copper oleate (equivalent to 50 p.p.m. of copper) was oxidized by the BS 148 method and time–sludge and time–acidity curves were plotted (Fig 24). It will be seen that in the initial period the rates of sludge and acidity formation were greater than the corresponding rates for the standard copper catalyst tests, but after longer periods the results for soluble and solid copper were approximately the same. It was observed that during the tests the blue colour of the dissolved copper gradually disappeared, the oil reverted to its natural colour, and a brown flocculent precipitate appeared. It was proved that dissolved copper

oleate rapidly decomposed when oil was heated to 150° C, the passage of air accelerating the process, and that all the copper appeared in the sludge. The high initial rate of sludge formation was obviously partly, but not wholly due to precipitation of copper compounds. This precipitation also raised the possibility that the catalysis might not be wholly due to soluble copper but also to the presence of dispersed particles of insoluble copper compounds.

These soluble-copper tests have recently been repeated on a current naphthenic-base oil containing in this case 0·2 per cent of copper oleate, equivalent to 200 p.p.m. of copper. In addition to the sludge and acidity the peroxide value and the exact amount of soluble copper were also determined. The peroxide values were most erratic and are not reported,

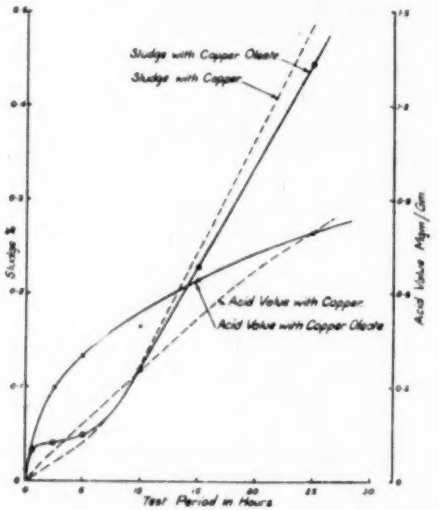

FIG 24

OXIDATION PRODUCTS—TIME CURVES FOR 1926 PARAFFINIC OIL USING METALLIC COPPER AND COPPER OLEATE (EQUIVALENT TO 50 P.P.M. OF COPPER) AS CATALYSTS—MODIFIED BS 148 OXIDATION TEST

the other results are given in Fig 25. It is interesting to note that the sludge curve for this naphthenic oil is very similar in form to that of the 1926 paraffinic oil, although the horizontal portion of the naphthenic oil curve extends from 8 to 16 hr, whereas that of the paraffinic oil curve lies between 2 and 5 hr.

Attention is particularly directed to the soluble-copper content of the oil. It will be seen that under these conditions of temperature and air access the bulk of the soluble copper is not stable in oil. It is likely that for longer periods than the limit of 45 hr shown the soluble copper will be well below 1 p.p.m. It is believed to be significant that the regions of rapid changes in slope of the copper-content curve coincide with those in the sludge and acidity curves. (It must be stated that the points shown on Fig 16 were the results of single determinations and not the average

of several determinations, as was the case for most of the other graphs. The smooth form of the soluble-copper curve is, however, evidence of the dependability of these results.)

The dependence of the soluble-copper content on temperature and oxidation is interesting when coupled with the results of a number of soluble-copper determinations made on oils withdrawn from transformers after varying periods of service. In no instance has any soluble copper been detected by a method capable of recording the presence of 0·05 p.p.m. of copper (possibly 0·01 p.p.m.). These oils were filtered before the copper

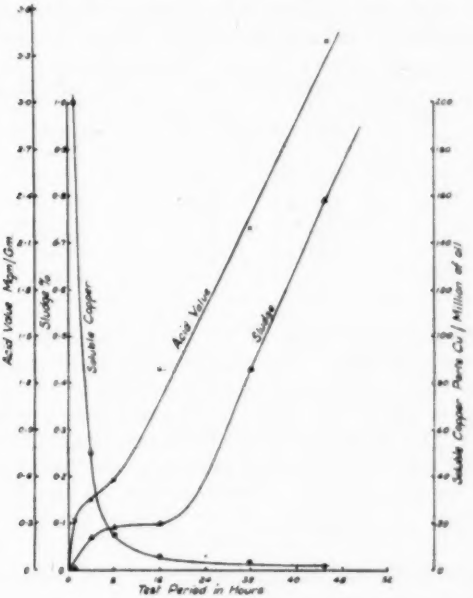

FIG 25

SOLUBLE-COPPER CONTENT OF THE OIL DURING PROGRESS OF MODIFIED BS 148 OXIDATION TEST CONTAINING ORIGINALLY 200 PTS PER MILLION OF SOLUBLE COPPER ADDED AS 0·2% OF COPPER OLEATE (OIL A2 NAPHTHENIC)

determination. In the unfiltered condition they contained up to 5 p.p.m. of copper as a result of the presence of this metal in the suspended sludge.

Some additional data were obtained during the copper-content tests, which it is more convenient to describe separately. In determining the sludge after various intervals in the original 1926 tests separate flasks were used for each time interval, and the sludge was precipitated from the oil in the usual manner with petroleum ether. The filtrates were then discarded. In the later tests it was desired to study the influence of the suspended matter, and this was done by returning to the oxidation flasks the filtered oils used for each point on the time–sludge curve and continuing the oxidation until the total of the two periods equalled 45 hr. Precipitation by petroleum ether was therefore not possible, and the oils were

accordingly filtered undiluted and cold. To obtain comparative results they were also filtered under the same conditions at the second filtration after 45 hr, but the 45-hr filtrate was finally diluted with petroleum ether to precipitate any sludge soluble in cold oil and again filtered. The results are given in Table X and yield a very definite conclusion : the removal of

TABLE X

Influence of Filtration of Oil at Various Intervals during Progress of BS 148 Oxidation Test using 200 p.p.m. of Soluble Copper as Catalyst

First oxidation period		Second oxidation period			Total sludge after 45 hr
			% sludge from :		
Time, hr	% sludge from cold, undiluted oil	Time, hr	Cold, undiluted oil	Diluted oil	
1	0·003	44	0·84	0·11	0·95
4	0·07	41	0·87	0·05	0·99
8	0·09	37	0·82	0·12	1·03
16	0·10	29	0·73	0·06	0·89
32	0·43	13	0·50	0·06	0·99
45	0·80	—	—	0·14	0·94

suspended matter at any stage of the oxidation does not influence the final result of the oxidation. The catalytically active materials are therefore oil-soluble. This conclusion is corroborated by other tests. In the accelerated tests at 150° C dry sludge powder was shown to be without catalytic power (Fig 3), and in the oil-immersed varnished-coil tests the filtered oil after contact with the coils was proved to oxidize very rapidly when oxidized, without the addition of any catalyst, in the BS 148 oxidation test.

Influence of Concentration of Soluble Copper and of the Oxides of Copper

The previous section indicates the need to study the behaviour of soluble copper at varying concentrations and also the need to extend the work to determine the catalytic behaviour of the copper oxides. The effect of varying the area of metallic copper in the BS 148 oxidation test has already been shown in Fig 17, which indicates that for the class B paraffinic oil examined, and under the test conditions specified, the amount of sludge and acidity formed are critically influenced at low values by the area of copper, but that above a limiting value the amounts become independent of area.

The influence of copper oleate, cupric oxide, and cuprous oxide was studied in a similar manner, *i.e.*, the BS 148 oxidation test was carried out on a class B oil (in this case a naphthenic type) containing varying proportions of these three compounds in place of metallic copper.

The sludge results are given in Fig 26. All three materials are shown to be strong catalysts. The curve for cupric oxide rises steeply with concentration and then becomes horizontal. Cuprous oxide exhibits an almost linear curve from 8 p.p.m. of copper to the maximum concentration in-

vestigated. Copper oleate shows a very steep initial rise, then a horizontal portion at about 0·73 per cent sludge, followed by a second rising portion and then a second horizontal portion at about 1·15 per cent sludge. It may be pure coincidence, but it is interesting to note that the two values for the horizontal portions of the curve approximate to the minimum and maximum scatter values obtained on this oil by the standard BS 148 method during a period when repeatability difficulties were being experienced.

The acidity results are given in Fig 27. Increase in catalyst concentration is accompanied by an increase in the amount of acidity formed up to a limiting figure for the catalyst of about 400 p.p.m. of copper. Beyond this concentration there is evidence of a constant acid value being reached. At all concentrations copper oleate gives the highest acidity and cuprous oxide the lowest, with cupric oxide lying between these two figures. The result of this selective action is to alter the ratio of acidity to sludge.

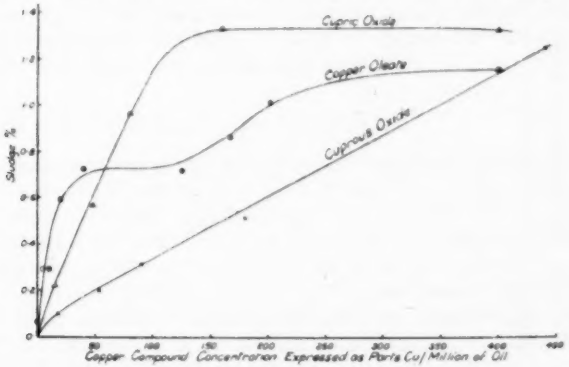

FIG 26

INFLUENCE OF CONCENTRATION OF COPPER COMPOUNDS ON AMOUNT OF SLUDGE FORMED IN MODIFIED BS 148 OXIDATION TEST. OIL A2

Taking the maximum values of the curves and assuming a mean molecular weight of 185 for the acids, the ratios of the percentages of acids to sludge are as follows : copper oleate 0·85 : 1, cupric oxide 0·80 : 1, cuprous oxide 0·4 : 1. In the standard BS 148 oxidation test on this oil the ratio was 0·57 : 1.

Several observations of practical importance can be based on these results. For example, during the machining and shaping of copper a dust containing the oxides of copper as well as finely powdered metallic copper is produced, and it is well known that the atmosphere of an electrical-engineering workshop contains substantial proportions of these materials. The entry of this dust into transformers is very likely, and the need to keep them clean during construction becomes of importance if danger to the oil is to be avoided. The presence of copper, even as low in concentration as 1 p.p.m. of oil, is sufficient to affect the oxidation rate of the oil.

In a transformer the amount of exposed metallic copper in the form of leads, terminal straps, and the like will normally be small, and is likely to be well below the critical ratio of 2 sq. cm. of copper per 100 g of oil. It follows that the deterioration of the oil will be strongly influenced by small

changes in the area of this exposed copper, and it is therefore well worth while to make every effort to limit this area. This consideration applies to the free bulk of oil in a transformer. The problem is complicated by the use of oil-impregnated coils in high-voltage transformers. If the insulation in these coils is porous a small volume of oil is in contact with a large area of copper conductor, and on first consideration the maximum copper effect might be expected. Oxygen access, however, is very limited, with the result that the copper influence is modified. Suitable paper insulation has also been shown to provide a barrier effect (Fig 8). The solution of copper by acid oil in the interior of a coil may not be immediately harmful because of the absence of oxygen, but it may prove ultimately harmful if, by a

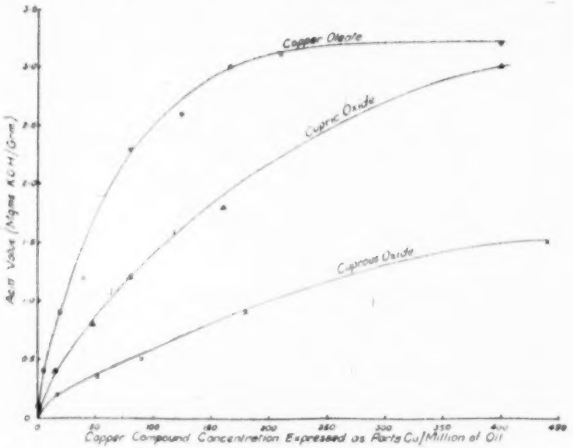

FIG 27

INFLUENCE OF CONCENTRATION OF COPPER COMPOUNDS ON AMOUNT OF ACIDITY FORMED IN MODIFIED BS 148 OXIDATION TEST. OIL A2

breathing mechanism, this dissolved copper is transferred to the main oil bulk, where oxygen access is not so restricted.

Green oil is occasionally met in transformers. This is obviously associated with the presence of soluble copper under conditions of restricted oxygen access and low temperature of operation. Transformers have been examined in which the oil in the middle of the coil was bright green, but the bulk oil surrounding the coil was dark yellow. The interior of the coil was free from sludge, but the exterior oil contained sludge in which a small percentage of combined copper was present. This illustrates the result of free oxygen access.

The results of Figs 26 and 27 also have a bearing on the controversy concerning the relative merits of metallic and soluble copper in the BS 148 oxidation test. These results prove that the rate of oxidation is dependent on the soluble-copper concentration, and since the precise form of the copper concentration–oxidation curves may vary with different oils, then the relative merits of several oils at one catalyst concentration may differ from their relative order of merit at another concentration.

On the other hand, with solid copper although the oxidation is critically dependent on copper area below a certain value, the knee of the curve for the oil examined is so far from the BS 148 specified test area that it is probable that even with substantial variations in the composition of transformer oils the test results will still lie on a portion of the curve remote from the range of critical dependence of oxidation rate on copper catalyst area. Therefore the use of metallic copper provides a far better chance of maintaining uniform catalyst activity at a non-critical easily controllable and uniform level than the use of soluble copper. There is, of course, a risk that one oil may be more influenced by metallic copper than another, but as copper is an essential material of construction, the susceptibility of an oil to catalysis by copper is a fair test.

Another disadvantage of soluble-copper compounds as catalysts is that their introduction into the oil also involves the introduction of a relatively large proportion of acid radicals of unknown and unpredictable effect on the oil. For example, for every 1 part of copper introduced as copper oleate, 9 parts of oleate radicals are also present.

Experiments with Varnished Copper Panels in Oil

The erratic influence exerted by varnish-impregnated coils on oil deterioration has been described in Part II. Whilst these tests resembled one practical form of varnish application, they gave no information on the barrier effect of fully baked varnish films used as surface-protective coatings. Moreover, so many variables proved to be present that little information could be derived concerning the mechanism of deterioration. It was therefore decided to make some tests on varnish films prepared on copper panels immersed in oil under more strictly controlled oxidation conditions. The method used was to oxidize the oil in the BS 148 oxidation-test equipment, using the copper catalyst as the metal test panel. The sludge and acidity developed were then considered to be measures of the barrier efficiency of the varnish. In addition, the amounts of copper appearing in the sludge and oil were likely to be of some importance.

The standard copper-foil catalyst was considered unsuitable on account of the risk of the sharp edges damaging the varnish film, and cylinders cut from copper tube of approximately 2 mm wall thickness were used of the same overall diameter and surface area as the standard cylinder prepared from copper foil. The end walls of these cylinders were radiused to eliminate sharp edges. They were coated with varnish by a double dip, drainage of the second coat being in the reverse direction to that of the first coat. During processing the cylinders were supported on crossed knife edges, the weak spots at the points of support being later given an additional dab of varnish. The total film thickness lay between 3·5 and 5 mil. Each coat of varnish was baked for 16 hr at 105° C which gave a fully baked film. Two series of oxidation tests were made on oil A2 (naphthenic base) in the presence of standard copper foil; bare cylinders prepared from copper tube; and cylinders treated with varnishes A4, C5, and D4. A blank test without any catalyst was also made. The varnishes were described by the makers as follows: A4 synthetic base, C5 natural resin oil, D4 natural resin–tung oil. In one series the temperature was held at

120° C for sixteen days, in the other at 150° C for 45 hr. At the end of these test periods sludge, oil acidity, soluble-copper content of the oil, and copper content of the sludge were determined.

The results at 120° C are given in Table XI. It will be seen that the sludge and acidity figures in the presence of varnished cylinders are nearly the same as those on the oil without catalyst. They are much lower than

TABLE XI

Characteristics of Oil and Sludge after Oxidation in Presence of Copper and Varnished Copper Cylinders for 16 *Days at* 120° C

(B.S. 148 test conditions except for time, temperature, and catalyst modifications)

Test on :	Sludge, %	Acid value, mg/g	Soluble Cu in oil p.p.m.	% Cu in sludge	Total Cu in :		
					Oil, mg	Sludge, mg	Oil and sludge, mg
Oil without catalyst	0·025	0·11	—	—	—	—	—
	0·020	0·11	None	0·01	None	0·002	0·002
Oil with standard copper foil	0·20	0·40	0·45	0·05	0·04	0·10	0·14
	0·18	0·40	0·45	0·05	0·04	0·10	0·14
	0·19	0·46	0·3	0·05	0·03	0·10	0·13
Oil with copper tube	0·15	0·33	0·3	0·06	0·03	0·10	0·13
	0·16	0·33	0·3	0·06	0·03	0·12	0·15
	0·15	0·33	0·3	0·06	0·03	0·10	0·13
Oil with varnished copper tube A4	0·026	0·11	0·45	0·14	0·04	0·035	0·07
	0·024	0·11	0·30	0·07	0·03	0·018	0·04
Oil with varnished copper tube C5	0·020	0·11	0·6	0·14	0·06	0·028	0·09
	0·027	0·11	0·3	0·08	0·03	0·023	0·05
	0·020	0·11	0·3	0·11	0·03	0·023	0·05
	0·027	0·11	0·3	0·11	0·03	0·030	0·06
Oil with varnished copper tube D4	0·039	0·11	0·2	0·08	0·02	0·030	0·05
	0·032	0·11	0·2	0·09	0·02	0·030	0·05
	0·039	0·11	0·2	0·08	0·02	0·030	0·05
	0·020	0·11	0·2	0·08	0·02	0·017	0·04
	0·018	0·11	0·2	0·09	0·02	0·017	0·04

those obtained on the oils containing bare copper catalysts. At the end of the test period all the oils contained soluble copper ranging in amount from 0·2 to 0·6 p.p.m. All the sludges contained copper in proportions ranging from 0·04 to 0·14 per cent. Calculating from these results, the total copper present in the oil and sludge (*i.e.*, the amount removed from the copper panel, and presumably taking part in the oxidation changes), the weights range from 0·04 to 0·14 mg.

In Table XII are given the results of the corresponding tests at 150° C (in this series only varnishes C5 and D4 were available). Varnish D4 is shown to be as effective at 150° C as at 120° C, but C5 is less effective at 150° C than at 120° C, although it still limits the extent of the oil deterioration. The amounts of copper in the sludge fall within the same limits

as those for the 120° C tests, and so do the soluble-copper contents of the oils containing bare copper. The oils containing varnished-copper cylinders do not, however, contain any soluble copper within the limitations of the analytical method used, which was capable of detecting amounts of less than 0·05 p.p.m. The total amount of copper in the sludge from the bare-copper experiments was much greater than in the 120° C tests, and reached 0·87 mg.

TABLE XII

Characteristics of Oil and Sludge after Oxidation in Presence of Copper and Varnished Copper Cylinders

(BS 148 oxidation test conditions (*i.e.*, 45 hr at 150° C) except for catalyst modifications)

Test on :	Sludge, %	Acid value, mg/g	Soluble Cu in oil, p.p.m.	% Cu in sludge	Total Cu in :		
					Oil, mg	Sludge, mg	Oil and sludge, mg
Oil with standard Cu foil	0·81	1·1	0·3	0·04	0·03	0·31	0·34
Oil with copper tube	0·72	1·0	0·5	0·11	0·05	0·82	0·87
	0·69	1·0	0·5	1·10	0·05	0·73	0·78
Oil with varnished copper tube C5	0·10	0·30	None	0·09	None	0·087	0·09
	0·11	0·35	None	0·07	None	0·075	0·075
Oil with varnished copper tube D4	0·018	0·11	None	0·06	None	0·012	0·01
	0·017	0·11	None	0·06	None	0·012	0·01
	0·028	0·11	None	0·07	None	0·020	0·02
	0·027	0·11	None	0·07	None	0·020	0·02

It should be noted that the original oil and the varnishes were examined and found to be copper-free. (The very small amount of copper found in the sludge from the blank oil test may have been dispersed in the original oil at a concentration below the limit of determination. The oxidation of this oil would result in the precipitation and concentration of this copper in the sludge, where it would be more readily detected.) Oxidation tests were also made on an oil in the presence of varnish films prepared on 1 mil tissue paper, and results obtained similar to those on the oil without catalyst.

The following tentative conclusions and comments are based on a consideration of the test results :—

(i) The sludge and acidity figures prove the barrier efficiency of the varnishes, but they also indicate that variations between varnishes are possible. The test method used may prove to be suitable as a simple means of evaluating varnishes for use as protective coatings on metal in oil-immersed equipment.

(ii) The varnish films were permeable to copper, but the amount transmitted was very small.

(iii) The amounts of copper in solution in the oils in the majority of the experiments varied within remarkably small limits, *i.e.*, 0·2 to 0·6 p.p.m.

The exceptions were for the varnished-copper tests at 150° C in which no soluble copper was formed. The limits in the immersed-coil test (Table IV) were of the same order, *i.e.*, 0·25 to 1·25 p.p.m., the greater values being observed to occur in oils of high acid value. The similarity of the results is striking in view of the different conditions employed in these tests.

(iv) The amount of copper in the sludge also varied within surprisingly small limits (0·04 to 0·14 per cent) with the single exception of the blank oil test. In the immersed-coil tests (Table IV) the limits were 0·05 to 0·3 per cent. These results suggested that copper was co-precipitated with sludge at a fairly constant rate, and even gave rise to the possibility that the acceleration of sludge formation by copper depended on the availability of sufficient soluble copper to maintain the copper concentration of the precipitating sludge at about 0·1 per cent.

This possibility is not, however, confirmed by the immersed-coil tests (Table III). The filtered oils from these tests when oxidized by the BS 148 method without catalyst yielded sludges up to 1·4 per cent, but as the filtered oils contained a maximum soluble-copper content of 1·25 p.p.m. the total amount of copper present was insufficient to permit the sludges to contain more than 0·0001 per cent of copper. It may be, however, that these oils contained dissolved varnish constituents from the " wet " varnish, and that these oxidized in the oxidation test to form a sludge. Unfortunately these questions were not obvious at the time of the immersed-coil tests, and no analytical data concerning copper contents are available.

(v) It would appear that at 150° C in the varnished-copper tests the rate of precipitation of the copper was greater than its rate of migration through the varnish film, whereas at 120° C the rate of migration was greater than the rate of precipitation. There certainly also appears to be a factor limiting the soluble-copper content of the oil in these tests.

It is appreciated that the work recorded concerning the behaviour of copper in oil is very incomplete, but it is hoped that the results are nevertheless of some interest.

Conclusions

In view of the length of this series it is desirable to recapitulate some of the more important conclusions.

Tests on Transformer Constructional Materials

The materials of construction of a transformer vary widely in their influence on the rate of deterioration of an oil. Many are almost inactive, but some accelerate and a few retard the normal rate of oxidation of the oil.

In the accelerated tests at 150° C copper and the copper-bearing alloys were outstandingly the most active catalysts. This was also true in the service-conditions tests at 80° C. The ratio of acidity to sludge varied with the test conditions. In general, as temperature and oxygen access decreased this ratio increased. It also changed with the nature of the material in contact with the oil, *e.g.*, on a class B oil the acid per cent/sludge per cent ratio in the presence of copper was 6 : 1 in the " service-conditions " test at 80° C and 0·5 : 1 in the BS oxidation test. At 80° C for all

materials other than copper it was 1 : 1. This ratio is likely to be greater for oil in transformers than is found in the BS oxidation test.

At the other end of the activity scale varnishes of the phenolic type were mild inhibitors of oxidation and reduced the rate of deterioration.

Copper conductors in a transformer coil are always covered. Their catalytic activity is modified by the nature and oil permeability of this covering.

Oil-resistant varnishes, when present fully baked films, do not cause oil deterioration, and the use is fully justified of protective coatings of varnish on oil-immersed metal equipment to act as a barrier between oil and metal. Varnish-impregnated coils, on the other hand, may cause oil deterioration and are erratic in their behaviour. This can probably be overcome by selection of varnish and processing conditions. One type of deterioration associated with varnished coils is probably a complex reaction involving the formation of copper compounds by interaction between "wet" varnish and copper, followed by a breathing mechanism which transfers soluble copper from the coil interior to the main bulk of oil, *i.e.*, copper and not the varnish is the direct cause of deterioration. Another type is the result of the solution by the oil of incompletely baked varnish resins, which subsequently become oxidized and precipitate as sludge.

BS 148 *Oxidation Test*

In spite of its many accepted limitations, the BS 148 sludge test gives as good an indication of the oxidation stability of an oil as any alternative test, and it has gained the confidence of the oil user. It is particularly valuable as a measure of the two oxidation products most harmful in a transformer, *i.e.*, sludge and acidity. Its repeatability is poor, but this criticism appears to be true of most oxidation tests. The causes of poor repeatability do not lie in the mechanical processes of separation of sludge from oil after oxidation, but in factors occurring during the oxidation in the test flask. Repeatability varies with different oils. Pre-war oils yielded, in general, more consistent results than wartime and post-war oils. There is some evidence to show that the vapour-phase conditions in the flask and reflux condenser air spaces are intimately connected with the difficulties experienced in securing repeatability—some oils are not affected by these factors, and in consequence yield consistent results. The repeatability difficulties are also associated with the temperature of the test. Many pre-war oils gave a straight-line sludge–temperature relationship, but post-war oils show a marked change in slope between 120° and 150° C. As the temperature of the test is increased beyond 120° C, the sludge–temperature curve begins to rise more steeply, the scatter of results increases, peaks appear in the acid value–temperature curve, and in general the oil becomes unstable and the oxidation is influenced by small unidentified factors.

For these reasons it would be preferable to carry out the test at 120° C. In the great majority of normally operated transformers this test temperature would be an adequate safeguard, but in a transformer liable to short-circuit conditions, small volumes of oil in contact with copper conductors may reach temperatures of the order of 150° C for short periods. If an oil

is liable to excessive breakdown at 150° C, then small quantities of catalytically active products produced under these conditions may be a danger to the main oil bulk. Until positive evidence is available regarding this risk the maintenance of the test temperature at 150° C is a reasonable safeguard.

Over a very long period (1926 to 1950) the sum of the percentage weight of acids plus sludge found by the BS 148 oxidation test on "finished" oils (*i.e.*, oils supplied to transformer users) has always fallen between the limits of 1·1 and 1·9 per cent. To avoid sludge troubles on the one hand and excessive acidity on the other, oils giving compromise values of sludge and acidity must be chosen. Normally operated transformers filled with class B oil selected on this principle have given excellent trouble-free performance.

Inhibited Oils

The development of inhibited oils is a subject of importance, but as uninhibited oils give satisfactory life and performance in normally operated transformers, the main application of inhibited oils seems to be for use in transformers operated under particularly severe conditions, *e.g.*, transformers designed for high-temperature operation, deliberately overloaded transformers, and those subjected to frequent short-period, short-circuit conditions. That is, their value will lie in their ability to minimize oxidation at high temperatures, say up to 150° C, and inhibited oils should be evaluated for stability at this temperature. Inhibited oils will also be of value for refilling transformers in which excessive oil deterioration in service has occurred.

Iodine Value as a Measure of Oxidation Stability

In an attempt to correlate the Wijs iodine value and the oxidation products of an oil as determined by the BS oxidation method it was found that all the oils examined of iodine value less than 1 gave negligible sludge, whereas all oils of iodine value greater than 5 yielded appreciable sludge. No relation was found between iodine value and the sum of the acidity and sludge.

Catalytic Influence of Copper Concentration

Copper in the metallic form and in the form of the oil-insoluble oxides and the oil-soluble organic compounds is an active catalyst for oil oxidation. Its activity is proportional to the area of the insoluble compounds or to the concentration of its soluble compounds when these areas or concentrations are small. Beyond certain limiting values the catalytic power becomes independent of area or concentration.

The metallic copper catalyst employed in the BS 148 oxidation test has an area well above the range of dependence of catalytic power on area. The concentration of soluble catalysts generally used in oxidation tests lies within the range influenced by concentration. The use of sufficient soluble catalyst to render the results independent of catalyst concentration would result in the unavoidable introduction of a large proportion of the acid radicals combined with the copper.

The presence of any copper compound in proportions as low as 1 part of copper per million of oil appreciably affects the rate of oxidation.

Permeability of Varnish Films to Copper

Thin films of baked varnish have been proved to be permeable to copper. If a varnish-coated copper test panel is immersed in oil, copper will migrate from the panel through the varnish film and appear as soluble copper in the oil. The amount is small and varies with temperature and the nature of the varnish. The subject is being further explored.

ACKNOWLEDGMENTS

The author expresses appreciation to Mr V. H. Howe, for helpful assistance and comments on engineering aspects of the problems discussed, and gratefully acknowledges the permission of the Electrical Research Association to include certain experimental results obtained while pursuing investigations sponsored by that body.

The author also wishes to thank Dr C. Dannatt, M.C., Director of Research and Education, and Mr B. G. Churcher, Manager of the Research Department, Metropolitan-Vickers Electrical Co. Ltd., for permission to publish this paper.

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VAPOUR PRESSURE OF LIQUEFIED GASES

SEVERAL laboratories in this country are now using the NGAA " Inverted Reid " procedure for determining the vapour pressure of liquefied gases, and this procedure is in fact under consideration by the Petroleum Gases Panel of Sub-Committee No. 3 as a possible IP Standard. The method involves the use of a bomb conforming to the general overall dimensions of the Reid bomb, but differs from the normal vapour-pressure procedure in that the large chamber (*i.e.*, the normal " air compartment ") is filled with the liquid sample, while the small chamber is used to provide ullage space, but contains only sample vapour and not air. For determining the vapour pressure of *butane* samples (at temperatures up to 45° C) it is normally safe to use a standard Reid bomb, but the Petroleum Gases Panel wishes to emphasize the dangers which can occur when using such a bomb for propane or propylene samples :—

(1) For conformity with IP 69/45, it is only required that a Reid bomb be tested to 100 p.s.i.g., and certain bombs therefore may not be safe for use with samples whose vapour pressures are of the order of 200 to 300 p.s.i. It is therefore essential that a suitable pressure test be carried out before a Reid bomb is used for C^3 samples.

(2) The above warning is obvious and probably unnecessary. A further source of risk, however, is less obvious. Thus, it may not be realized that in the Reid bomb with a volume ratio of 4 to 1 between the two chambers, the expansion of the liquid already filling the large chamber, could, under certain circumstances, be so great as to exceed the available free volume of the small compartment, with consequent risk of bursting the bomb due to hydrostatic pressure. This applies particularly to propylene samples, if they are cooled, on charging, to a temperature near the boiling point of propylene and then warmed in the bomb to the normal test temperature of 45° C (113° F). Users of this method are therefore strongly warned to avoid excessive cooling of such samples when charging the vapour-pressure bomb.

The Petroleum Gases Panel is considering the design of a modified bomb, of light weight, in which the volume ratio between the two compartments will be such as to eliminate this danger.

J. H. D. HOOPER
Chairman—Petroleum Gases Panel

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Oilfield Exploration and Exploitation

Geology

1236. Resistivity of brine-saturated sands in relation to pore geometry. W. O. Winsauer, H. M. Shearin, Jr., P. H. Masson, and M. Williams. *Bull. Amer. Ass. Petrol. Geol.*, 1952, **36** (2), 253.—Although much progress has been made during the past decade in various phases of reservoir engineering, a commonly occurring hindrance to the formulation of quantitative relationships has been uncertainty about the effects of rock texture.

A concept which has made a periodic appearance in geological literature is that of the tortuosity of pore channels. In the present paper a method has been devised for the direct determination of the tortuosity of pore channels in porous rock. The tortuosity, a geometrical parameter, together with the porosity, determines the resistivity factor. Experimental determinations made on a suite of sandstone samples selected to cover a wide range of texture have shown that: (1) tortuosity values were lower than had been previously supposed; (2) the resistivity factor is related to porosity and tortuosity; (3) the resistivity factor correlates with the packing index; and (4) the resistivity factor can be approximated by means of a relation involving only resistivity factor and porosity.

In discussing the petrophysics of limestones, it is desirable first to classify them in a manner to portray as much as possible the essential pore characteristics of a reservoir. When correlating quantitatively drill cuttings with so-called " indirect " methods, it is necessary to study the pore structure in detail.

Limestone reservoirs found at increasingly greater depths, with accompanying higher cost of production per well, have made the problem of determining net pay thickness of limestone reservoirs more exacting. In discussing the petrophysics of limestone, it is necessary first to classify them in a manner to portray as much as possible the essential pore characteristics of a reservoir.

A skeleton classification with symbols is presented and co-ordinated with petrophysical data, such as porosity, permeability capillary pressure, and electrical resistivity of water-bearing and oil-bearing limestones. E. N. T.

1237. Grain-size distribution and reservoir-rock characteristics. J. C. Griffiths. *Bull. Amer. Ass. Petrol. Geol.*, 1952, **36** (2), 205. (*Symp. on Oil and Gas Reservoirs, AAPG., St Louis, Apr.* 1951.)—It has previously been pointed out that a sediment possesses two primary properties, mineral composition and texture, and this paper deals with one of the textural properties, namely grain-size distribution and its application to reservoir behaviour and performance.

The grain-size distributions of oil-reservoir rocks may be classified in four groups: arkose, low-rank graywacke, orthoquartzite, and quartzose graywacke types. Limestone and the rare high-rank graywacke oil-reservoir rocks are omitted from consideration.

By using variations in grain-size distributions as indicators of the varying proportions of mineral constituents, particularly the clay fraction, it can be shown that there is a predictable relationship between clay content and the self-potential curve of the electric log. Similarly, the grain-size distribution when coupled with its implications in terms of proportions of mineral constituents may be used to recommend improvements in completion procedures in terms of gravel pack and slotted-liner practice.

The relationship between grain-size distribution and fluid saturation has been

investigated in the laboratory, and results in the field show a parallel relationship; in both cases there appears to be a traceable relationship between grain-size distribution and oil–water saturation in sandstone reservoirs.

On the basis of these findings it seems clear that grain-size distribution, suitably qualified by its inter-relationship with proportions of mineral constituents, is a useful measure of petrographic properties of reservoir rocks and forms a basic quantitative measure of empirical comparison between petrographic and reservoir characteristics in oil-producing reservoir rocks. E. N. T.

1238. Stratigraphy and structure of the Spraberry trend. J. H. Bartley. *Oil Gas J.*, 6.12.51, **50** (31), 101.—The term "Spraberry" covers that group of Lower Permian sandstones of lower Leonard age occupying the Midland Basin and certain portions of the Eastern Platform area of West Texas. In the type locality (Spraberry Deep field, Dawson County) the Spraberry consists of an upper and a lower sand, each about 300 ft thick, separated by 250 ft of mainly shaly limestone. The so-called "sands" are in fact siltstones.

Productive structures are of two main kinds: west plunging monoclinal noses with little closure but with permeability pinch-out providing satisfactory traps, and anticlines due to compaction around reefs in the underlying Pennsylvanian and Ellenburger limestones. Eastward the Spraberry grades into limestones, westward into shales. An important factor is the fractured condition of the sands, believed to be due to movements in late Permian times. J. C. M. T.

1239. The jet sampler—a method of obtaining submarine samples for geological purposes. K. W. Barr. *J. Inst. Petrol.*, 1951, **37**, 658–61.—The equipment described affords a method of obtaining bed-rock samples from below recent mud deposits in offshore areas. A. R. W. B.

1240. Relation of fractures to accumulation of oil. G. R. Gibson. *Oil Gas J.*, 29.11.51, **50** (30), 107.—The commonest Spraberry rock types are siltstones, with a grain size around 1/45 mm, and shales. Production is virtually dependent on fractures which are near vertical but the exact pattern of which is as yet unknown. Some fractures extend vertically as much as 100 ft. Permian movements are not considered sufficient to account fully for the fracturing, which is more likely due to post-depositional contraction (especially differential contraction between the shales and the siltstones), as a result of mild metamorphism beneath the 7000 ft of cover. Fractures are wider in the shales than in the siltstones. J. C. M. T.

1241. A new technique in preparation of cores for preservation and study. E. D. Patterson. *World Oil*, 1.2.52, **134** (2), 74.—A new technique is described for preparing cores for study and preservation. The cores are slabbed longitudinally, and a segment approx 1 inch thick is preserved for study. The surface of the slab is treated with 10% HCl, washed, dried, and painted with a clear lacquer. The lacquer gives a permanently wet appearance to the slab, enabling the petrography of the rock to be more easily seen. C. A. F.

1242. Core-analysis practices—basic methods and new developments. T. A. Pollard and P. P. Reichertz. *Bull. Amer. Ass. Petrol. Geol.*, 1952, **36** (2), 230.—Describes some of the classical core-analysis procedures and lists particularly some of the more recent developments which the writers feel are of interest to petroleum geologists. These developments pertain not only to the ever-present question of accurate reserve estimation but also to the recognition of petroleum-bearing rocks and the selection and evaluation of those which will produce oil into wells, as well as the many properties which will help in determining the proper completion and producing practices.

Discussion is divided arbitrarily on the basis of conventional core analyses and large-core analyses. By conventional core analyses the writers mean analytical procedures performed on small plugs cut from whatever types of oil-well cores may be submitted to the laboratory. By large-core analyses is meant analytical procedures performed on complete cores or large segments of them as received in the laboratory. E. N. T.

1243. Reef found in Oklahoma Panhandle. P. C. Ingalls. *Oil Gas J.*, 13.12.51, **50** (32), 137.—A wildcat sunk by Flynn Oil Co. in Beaver County, Oklahoma, has produced an estimated 50 brl/hr of high-gravity water-free oil in a drill-stem test over a 10-ft interval at a depth of 5554 ft. Core samples indicate that the horizon is a Pennsylvanian Reef Limestone comparable in age to that found in Scurry County, Texas. Gas and oil were also encountered in other highly porous horizons between 4750 ft and total depth. J. C. M. T.

1244. Lost Soldier field, Wyoming. R. L. Pott and S. F. DeVore. *Oil Gas J.*, 21.1.52, **50** (37), 80. (*From Guide Book of 6th Annual Field Conf.*)—Lost Soldier field is 35 miles N.W. of Rawlins, Wyoming, and lies at the edge of the Separation Basin. The field is an asymmetric anticline trending N. 25° W., representing a major fold along the northern rim of the Great Divide Basin. There is a gradual thickening of the strata from north to south independent of structure, Production ranges from the Cambrian to the Frontier sand.

Cumulative production to date of this thirty-five-year-old field is 45,000,000 brl, and estimated ultimate recovery is over 100 million brl. J. C. M. T.

1245. Another field for Alabama. P. C. Ingalls. *Oil Gas J.*, 4.2.52, **50** (39), 109.—A discovery well has been completed which indicates a fourth commercial oil pool for Alabama in Escambia County, a few miles north of the Florida Panhandle. This discovery considerably extends the limits of production in the deep salt basin of S.W. Alabama. The well was completed in a 25 ft thick oil sand of Upper Cretaceous age at 5944 to 5949 ft. J. C. M. T.

1246. Dome interest revived. Anon. *Oil Gas J.*, 21.1.52, **50** (37), 58.—Recent discovery of a commercial oil pool on the Glazier salt dome in Perry County, S.E. Mississippi, may bring about a revival of flank drilling on over forty known salt domes in this state, especially those which encounter the Upper Cretaceous Eutaw and Tuscaloosa sands. Glazier is the first piercement-type salt dome in Mississippi to produce commercial quantities of oil. J. C. M. T.

1247. New Mexico discovery made. Anon. *Petrol. Engr*, Jan. 1952, **24** (1), B94.—1 H. L. Lowe, Lea County, New Mexico, was completed for 385 b.d. of 38·2° oil from 10,126 to 10,136 ft. G.O.R. was 734 : 1. The well is in the Wolfcamp region. C. A. F.

1248. Continental gets producer in West Texas County. Anon. *Petrol. Engr*, Dec. 1951, **23** (13), B90.—A well in Hidalgo County, Texas, was completed at 8935 ft for 3,955,000 cu. ft/gas/day and 146 b.d. of 56·8° distillate. G.O.R. was 30,000 : 1. C. A. F.

1249. Oil on Williston's rim. Anon. *Oil Gas J.*, 25.2.52, **50** (42), 113.—1 East Poplar rig has shown 4150 and 3200 ft of 38° gravity oil on two drill-stem tests in the Mississipian–Charles Limestone at about 5680 ft. This wildcat, 30 miles north of Shell's 1 Northern Pacific in the Richey area (first well to find oil in the Montana segment of Williston Basin), is now drilling ahead below 9000 ft. J. C. M. T.

1250. Utah gas well completed. Anon. *Petrol. Engr*, Dec. 1951, **23** (13), B90.—1-AHL Rath, Emory County, Utah, produced 3,500,000 cu. ft/day from 2690 to 2700 ft. Further production is expected at a lower horizon. C. A. F.

1251. Big Utah gas strike made. Anon. *Petrol. Engr*, Dec. 1951, **23** (13), B90.—1 Utah Fuel Company, Carbon County, Utah, produced on test 9,120,000 cu. ft. gas/day from the Morrison at 4692 to 4761 ft. The well is to be connected to a pipeline from Moab to Salt Lake City. C. A. F.

1252. New California field open. Anon. *Petrol. Engr*, Jan. 1952, **24** (1), B94.—1 Rynne Fisher, approx 2 miles northwest of the Honor Ranch field in Los Angeles County, California, was completed for a flow of approx 5000 b.d. of 32° clean oil. Pay is between 4610 and 4724 ft. C. A. F.

1253. Calmar development test opens D-3. Anon. *World Oil*, 1.2.52, **134** (2), 240.—A well in the Calmar sector between Leduc and Wizard Lake, Alberta, has found 415 ft of D-3 pay, the third thickest pay found in the state.

South Calmar 3-2, which found 80 ft of D-2 pay and 17 ft of D-3 pay on test from 5949 to 5969 ft, flowed gas at 345,000 cu. ft/day and recovered 1260 ft of gassy oil.

C. A. F.

1254. British Columbia well. Country's first oil. Anon. *Petrol. Engr*, Dec. 1951, **23** (13), B92.—The first well to find oil in British Columbia, the Allied Fort John 1, was completed in Permo-Pennsylvanian limestone. On test gas was recovered in 4 min from 5633 to 5655 ft and 125 ft of gassy mud, 900 ft of light oil, and 480 ft brine were recovered in 90 min.

The well is in the Peace River area. C. A. F.

1255. Saskatchewan hits. Anon. *Oil Gas J.*, 21.1.52, **50** (37), 54.—The wildcat Socony Western Prairie 1 Roseray, 35 miles N.W. of Swift Current, Sask., is reported to have flowed 675 b.d. of 24° gravity oil from zones between 3065 and 3126 ft. This is the first commercial show of medium-gravity crude in Saskatchewan, which at present produces heavy crude from Coleville and Lloydminster fields. The well was sited on a structure located by seismic survey and structural drilling. The producing formation, believed to be the Lower Cretaceous Blairmore, is a sand divided by non-porous layers.

It is planned to drill the well 500 ft deeper into the Jurassic. J. C. M. T.

1256. Mexican oil discovery. Anon. *Petroleum*, Mar. 1952, **15** (3), 74.—Two important new fields have been discovered in Mexico, one at Tamiahua, near Tampico, and the other in the Tehuantepec isthmus. C. A. F.

1257. New Colombian strike. Anon. *Oil Gas J.*, 6.12.51, **50** (31), 82.—The International Petroleum Co. of Colombias' Totumal wildcat has flowed 550 brl of 25° gravity crude through a ½-inch choke in a 12-hr test. The producing section was a fractured limestone and shale of Cretaceous age at a depth of 6740 to 7215 ft. The well is situated in the middle of the Magdalena Valley, 75 miles north of the former De Mares concession, where exploration was suspended last August. The well will probably be drilled deeper. J. C. M. T.

1258. Ainsdale test is stopped; site for new try chosen. Anon. *World Oil*, 1.2.52, **134** (2), 246.—A well drilled near Ainsdale, Lancs, has been abandoned as dry at 4353 ft. Geological data obtained have, however, encouraged further drilling, and a new site has been chosen. Aim is to find source of shallow production at Formby.

C. A. F.

1259. Dutch oil discovery. Anon. *Petrol. Engr*, Dec. 1951, **23** (13), B92.—Commercial gas has been found near Tubbergen in Overijssel, Holland. The discovery was drilled on an anticline trending eastwards from Ommen into Germany. Productive area was reported to be approx 18,000 hectares. C. A. F.

1260. French company reports two successful wells. Anon. *Petrol. Engr*, Dec. 1951, **23** (13), B90.—It is reported that oil has been found in a well on the banks of the Ogowe River, 75 miles northeast of Lambarene in French Equatorial Africa. Production was 16 b.d. plus water from sands at 3445 and 3540 ft.

Productive deep formations are reported from Lacq in the Pyrenees foot-hills; Lacq 3 produced over 100 brl/hr of good-gravity oil from 11,440 to 11,506 ft.

C. A. F.

1261. A contribution on the Limagne bitumens. M. Louis and F. Bienner. *Rev. Inst. franç. Pétrole*, 1951, **6** (12), 413–20.—The numerous bitumen occurrences in the Limagne have long been known, but their origin and bearing on the search for oil are uncertain. The Limagne shows evidence of a subsiding trough formed in the Oligocene. Depression is greater in the west than in the east. On the basement at the base of the deposits is an arkose of variable thickness, which diminishes from north to

south. There are also fine sands and thin shale beds with small amounts of pyro-bituminous material. 200 to 400 m of Middle Stampian overlies these, and at the base it is lagunar, becoming brackish-lacustrine above. Locally the lagunar Middle Stampian seems to have given favourable or nearly favourable conditions for oil formation. The bitumen indications associated with this stage are connected with faults or with the reservoir sands. There are also shows near volcanic manifestations. The bituminous impregnations in the Chattian limestones at Pont-du-Château are secondary. The Chamalière arkoses are probably impregnated with bitumen by lateral migration from Stampian lagunar impregnated sands. Only the Crouelle well has found crude oil, and this is light and attributed to volcanic action on the bitumen.

Three thin asphaltic sandstones occur in an outcrop of Lower Stampian sandstones at Puy Saint-Romain. The upper bed had 3 to 4% of hard black bitumen soluble in chloroform, and acting as a cement for the mineral grains. The bitumen is low in oily constituents. The sulphur content is as much as 11·22%. The sand had organic matter which was insoluble in chloroform, but partially soluble in acetic acid. This was separated into brown and grey parts which differed mainly in their oxygen and sulphur content. These substances seem to have been changed towards petroleum. 10 kg of the sand after extraction of the bitumen was heated at 500° C, giving 47 gm of oil, 143 gm of water, while the gas and losses totalled 165 gm. The oil had traces of phenols, and smelled of ammonia, pyridine, and H_2S. After removal of organic bases the oil had 11·22% of sulphur, and 61·8% of this oil distilled below 300° C. Little of the original nitrogen remained in the oil. Some of the data for the Chamalières arkoses are similar to those described for Puy Saint-Romain. The organic matter insoluble in chloroform in both instances has an elementary composition similar to that given by Trask for the organic matter in ancient sediments. The presence of bitumen in the same rocks suggests that crude oil is not an intermediate stage between these two substances.

The various bitumens of the Limagne area seem to be related. G. D. H.

1262. Po Valley commercial oil deposits called likely. Anon. *World Oil*, 1.2.52, **134** (2), 244.—A well in the Cortemaggiore field in the Po Valley, Italy, is reported to have reached important " structures " at 11,480 ft. Max gas potential in the valley is approx 353,199,000 cu. ft/day from over 100 wells, but approx one-third only is produced. C. A. F.

1263. Kuwait oil discovery. Anon. *Petroleum*, Mar. 1952, **15** (3), 76.—Magwa 1, 7 miles north of the tip of the Burgan field, has found oil; it is uncertain whether this is an extension of the field. C. A. F.

1264. Nigeria's first wildcat drilling below 4600 ft. Anon. *World Oil*, 1.2.52, **134** (2), 242.—A wildcat near Owerri in eastern Nigeria was spudded in October 1951 following extensive exploratory work in the area. Depth of well is below 4600 ft. C. A. F.

1265. East Pakistan oil test approaching its objective. Anon. *World Oil*, 1.2.52, **134** (2), 246.—A test well in the Patharia hills in Eastern Pakistan has reached 5000 ft. Numerous dry gas shows have been found under high pressure. C. A. F.

Geophysics and Geochemical Prospecting

1266. Airborne profile recorder. J. H. Cornell. *World Oil*, 1.2.52, **134** (2), 223.—The use of a new instrument, the Airborne Profile Recorder (APR), is described. It is an airborne electronic instrument which can produce an accurate elevation profile record along a selected line. The equipment has been developed from the radar altimeter.

The method has been of great use in providing ground control points of known elevation so that contour lines may be drawn directly from aerial photographs. The margin of error is only 20 ft. C. A. F.

1267. Geophysical surveys on the Bahama Banks. C. S. Lee. *J. Inst. Petrol.*, 1951, **37**, 633–57.—Geophysical methods employed in the great areas of shallow water on the Bahama Banks are reviewed. Previous geophysical and geological work through-

out the region is discussed and related to the most up-to-date work in Abaco, Eleuthera, and Ragged Island. As a result, explanations of structural build-up and processes of sedimentation are advanced which differ from previous explanations.
A. R. W. B.

1268. New aids for seismologists. P. C. Ingalls. *Oil Gas J.*, 29.11.51, **50** (30), 139.—Lack of knowledge of lateral velocity variation in beds leads to anomalous results in seismic work, but the necessary surveys are rarely carried out. A cheaper method than the standard one is performed by exploding dynamite caps in shallow wells, with geophones placed on the surface. Using standard perforator guns firing bakelite bullets, velocity surveys down to 5000 ft can be carried out, and further development may extend this limit to 10,000 ft.

Two oil companies have produced independently two well-bore velocity-logging instruments giving accurate velocity measurement of rocks encountered in a well by small (1- and 5-ft) intervals. J. C. M. T.

1269. Scale model experiments in electromagnetic methods of geophysical exploration. A. R. Clark and A. G. Mungal. *Canad. J. Phys.*, 1951, **29**, 285.—A method is described of accurately measuring the phase as well as the amplitude of alternating magnetic fields of small amplitudes. The method has been applied to the response of conducting bodies placed in an electromagnetic field, and the results indicate how the position, dimensions, and dip of buried conductors may be evaluated. S. B.

Drilling

1270. Canada's subzero temperatures create complex problems. D. J. Elliott. *World Oil*, Dec. 1951, **133** (7), 115.—Subzero temp are not new to oilfield operators; conditions in these fields of 20° below zero have, however, to be anticipated for at least six months of the year. Freezing of drilling tools, mud pits, and general line communication delays operations considerably, but in addition freezing of blow-out preventers and other safety devices greatly increases operational hazards. Steam drilling is not usual in the Canadian field, and it was necessary therefore to obtain portable steam generators, of the flash-generator type, for de-icing drilling and production equipment. A. J. H.

1271. Analysis of rock bit performance data. H. B. Woods. *World Oil*, Sept. 1951, **133** (4), 193.—Erroneous conclusions drawn from data of bit performance may be avoided by adopting a graphical method, as outlined, from which may be made comparisons of bit quality and estimation of the optimum time at which a bit ceases to be efficient. Drilling costs are analysed, with reference to specific examples. A. J. H.

1272. A drillability classification of geological formations. A. L. Head. *World Oil*, Oct. 1951, **133** (5), 125; *Proc. Third World Petrol. Cong.*, 1951, **2**, 42–57.—The cost of drilling a well is approx 75% of the total cost, and it may be said therefore that a reduction in drilling time, resulting from more accurate selection of bits, would greatly reduce overall expenses. Although bits previously have been loosely qualified as soft- or hard-formation bits, etc., this classification is to be based on more accurate scientific investigation. Factors affecting the rate of penetration include: formation, type of bit, wt on bit, rotational speed, hydraulic action, size of hole, and efficiency of personnel and equipment. The drillability test bit differed from actual bits in that the central, and efficient, portion of the bit is omitted, this section of the core being first drilled out by a diamond-core bit; the construction of the test bit is such that the rollers may be easily replaced. The apparatus was adapted from a standard lathe, the bit being held in the tailstock.

Having fixed a rotational speed of 110 r.p.m. and thrust of 417 lb, the time required to drill $\frac{1}{10}$ inch, expressed in sec, was referred to as the D.C.N. (Drillability Classification Number). Comparing test results with actual field results, and different bits, it was shown that the D.C.N. was consistent. It was not possible to establish any hardness D.C.N. relationship. Data and references. A. J. H.

1273. Drilling and completion practices in the Church Buttes field. W. C. Dinger. *World Oil*, 1.7.51, **133** (1), 178. (*Spring Mtng, API Casper.*)—Producing horizons are at 12,433 to 13,053 ft, and the production, ranging from 3 to 15 million cu. ft/day, is at a flowing pressure between 3000 and 4500 p.s.i. Liquid content is 6 to 8 brl/million cu. ft.

Drilling procedure, which is relatively straightforward, is explained and a general geologic introduction given. The field was discovered by seismic survey in 1941, but the discovery well was not drilled until April 1946. A. J. H.

1274. Sonic drilling predicted. Anon. *Oil Gas J.*, 23.8.51, **50** (16), 103.—President of the Ultrasonic Corp., Cambridge, Mass., states that research is taking place on the subject of a high-frequency, sonic-vibrated, non-rotary blunt drilling tool. If developed it would be as effective as a conventional rotary tool, but rarely requires withdrawal from the borehole for sharpening, etc. J. C. M. T.

1275. Simplified departure curves. L. de Witte. *Oil Gas J.*, 11.2.52, **50** (40), 117.—Discusses the use of " simplified departure curves " in which apparent resistivities are plotted against either invaded-zone or true resistivities for various fixed values of the ratios' electrode spacing, or invasion dia, over hole dia. In practice, an infinite number of possible solutions, termed " equivalent combinations " for values of true and invaded zone resistivity and invasion dia is possible, and it is shown that no number of additional observations within the scope of conventional electrode spacing is capable of resolving which of the possible combinations is present. The errors resulting from neglect of this equivalence principle are likely to be greatest in all cases where invasion dia are small. Very long normal and lateral spacings (when the apparent approaches the true resistivity) give the best resolution, but their use is limited by bed thickness and boundary effects. The Laterolog and Induction log are capable of giving unique solutions for the unknown parameters in certain particular cases. J. C. M. T.

1276. New automatic drilling control. R. F. Carlson. *Oil Gas J.*, 11.2.52, **50** (40), 98.—This control unit, developed by the Texas Flange Co., is of the constant-weight type and is designed to fit between the drum shaft and auxiliary brake of existing draw works with the min of alterations. Step-up gearing from the drum shaft drives a hydraulic pump, the output from which is restricted by a valve, air-operated in accordance with the dead-line tension. As the tension increases, so the valve opening is reduced and the increased back-pressure on the pump reduces the rate at which cable is payed out by the drum-shaft. Provision is made for motoring the pump when very light drill strings are in use. Speeds from 0 to 75 ft/hr are accommodated, and the max drill-pipe load recommended is 240,000 lb. J. C. M. T.

1277. Latest applications of diamond coring. R. W. Stuart. *World Oil*, Sept. 1951, **133** (4), 173.—Recently, continuous coring of geologic formations has increased rapidly in importance, a recovery of almost 100% providing the geologist with complete information on the formation. This has been well demonstrated in the diamond coring of the recently discovered Spraberry sand, which originally was believed to be unproductive commercially, as suggested by the other tests; in fact, it has commercial possibilities. Deep formations are expensive with any drilling method, but the reliability of diamond coring, also for making full hole, has greatly encouraged the use of this method. The use of cheap diamonds has been shown to be at least as effective, if not more so, than that of the more expensive diamonds. Technical aspects are discussed. A. J. H.

1278. Spraberry innovations. R. F. Carlson. *Oil Gas J.*, 4.2.52, **50** (39), 37.—Special conditions in the Spraberry have led to various new drilling techniques. High-angle deflected drilling has been tried with a view to cutting across a greater number of the Spraberry's fractures and so enhancing production. In some cases four " drain holes "—short, virtually lateral holes off the main well within the producing section—are drilled, using a special form of whipstock and flexibly-jointed drive pipe.

A new form of diamond drill has been developed which enables cores to be taken without pulling the drill pipe. The main bit is hollow, but for normal operation the hole is filled by a subsidiary bit so that a full hole is drilled. When it is required to

core, this central bit is removed by a wire line and replaced by a core barrel which receives the core cut by the hollow outer bit.

A tool used to help reduce pressure on the formation when drilling in, and to reduce lost circulation, is included in the drilling string and contains upward-directed jets which by-pass a portion of the drilling fluid and help to lift the used fluid on its way up between the drill pipe and the hole. J. C. M. T.

1279. Wilshire conducts second Spraberry air drilling venture. O. H. Berry and W. Queensbury. *World Oil*, Dec. 1951, **133** (7), 126.—No claim is made to the effect that air drilling is the optimum method in this region, but its use in overcoming lost-circulation problems, and in drilling through depleted or semi-depleted reservoirs for core studies, is important. The first well was barren, but in the second attempt oil is being continuously jetted from the well at the rate of about 10 brl/hr. No tendency has occurred for plugging of the tubing, although some bits were plugged after running to bottom. The introduction of three valves in the drill string has facilitated the removal of accumulated oil. Air-drilling hazards are not in excess of those associated with conventional rotary drilling methods. A. J. H.

1280. Air drilling the Spraberry sand. O. H. Berry. *World Oil*, Sept. 1951, **133** (4), 169.—Drilling fluids used with rotary rigs have included water, complex colloids, oil-base muds, natural gas, as in the San Juan field, on which the particular operations were based, and air as on the Martin County, Texas field. It was considered that the use of air in the exploratory well Ruby Ragland 1 would facilitate the estimation of the natural productivity of the sand, although this particular well did not give commercial production. The use of reverse circulation gave a cleaner hole, and more accurate correlation of geologic samples with depth. On some occasions small amounts of fluid entering encouraged the adhesion of particles to the pipe wall. A. J. H.

1281. A new stimulation technique. J. M. Moore and J. C. McCormick. *Oil Gas J.*, 29.11.51, **50** (30), 102.—A new method of well stimulation has been tried with success in eight wells of the Greater Spraberry field, Texas. The process uses an acid–kerosine gel of such stability that various solids (such as sand) and chemical agents can be added in quantities to suit particular conditions. This material, called Jel × 500, is pumped into the producing formation, where it dissolves out calcareous material, silicates, and hydrocarbon residues, extending existing fractures and forming new ones while the suspended sand serves to keep fractures open. The injection is performed similarly to acidizing, beneath a packer, and oil is used for displacement. J. C. M. T.

1282. Down-the-hole pressure surges and their effect on loss of circulation. W. C. Goins, J. O. Weichert, J. L. Burba, and D. D. Dawson. *World Oil*, June 1951, **132** (7), 107. (*Spring mtng of S.W. District of API Divn of Production, Beaumont, Texas.*)—The large number of cases of lost circulation necessitated an investigation of the causes; "balled" collars contributed largely, and it was concluded that preventive measures would adequately reduce losses in circulation. Of the effects of pipe movement, no information had been available, and it was decided to investigate this effect by attaching a sub in place of the bit, and to instal a pressure recorder ahead of the sub. Two ¼-inch ports in the sub permitted circulation.

Readings were taken on a continuous recorder in the mud pit, and the hole pressure was recorded in the normal way. It was concluded that pipe movement has an appreciable effect, and was more critical with the use of high-density mud. This is particularly important when the bearing power of the formation approaches the pressure due to the hydrostatic head of mud; this point arises in deep wells, in which heavy mud is used. Rapidly opening the mud pump may also give rise to significant pressure surges. A. J. H.

1283. Performance and accuracy of Amerada bottom hole pressure recorder with special reference to use in drill stem formation tests and repeatability of reservoir pressures obtained therein. A. Laird and J. Birks. *J. Inst. Petrol.*, 1951, **37**, 678–95.—A technique has been developed for the use of the Amerada type RPG-3 gauge by which pressures can be determined with an accuracy of better than ±0·05% of the full-scale value for any individual pressure element. This has been achieved using a

diamond-pointed stylus on black paper which gives lines of 0·0005 inch thickness. Before a pressure element is put into use a detailed laboratory investigation is necessary to determine the variation of the temp coeff with pressure and the hysteresis curve for the element. The pressure-deflection characteristics of a gauge change with use, and it is necessary to bracket the unknown with standard pressures using a dead-weight tester. The pressure is computed from the deflections, using the method of proportionation, and corrected for temp and hysteresis. A. R. W. B.

1284. Controlled tong torque increases drill collar service. Anon. *World Oil*, Nov. 1951, **133** (6), 127.—In the first year of its application the tong contributed to a reduction in time of 77% for fishing for drill collars. The two extreme cases of joint make-up are undesirable, since in over-straining the tooth form of the joint is much distorted, whereas when loose, " wobble " occurs, with resultant wash-outs and failure. The torque indicator, which operates through a compressed fluid to a Bourdon Gauge reads directly in lb for the estimation of the torque transmission. Tentative data have been put forward by manufacturers for the limits of torque, but the number of variables is large; the type of lubricant used plays an important part. Extent of wear, and dimensions of pipe and collars are both relevant to torque functions. A. J. H.

1285. Time-dependent strains around uncased holes. A. D. Topping. *World Oil*, 1.7.51, **133** (1), 134.—A survey of reports on wells which have collapsed after a certain period of drilling led to the possibility of a time factor being involved. A mathematical treatment is given to the consideration of this problem from the standpoint of creep of rocks. References. A. J. H.

1286. A review of casing string design, principles, and practice. Pt I. J. O. Hills. *World Oil*, 1.7.51, **133** (1), 113. (*Spring mtng, Pacific Coast District, Div of Production API, Los Angeles.*)—Design is frequently more stressed in the case of deep wells, but economic considerations require also the careful design for medium-depth wells. The time and expense involved in the designing of a casing string are small in comparison with the cost of a casing operation, and particularly in the case of combination strings are fully justified.

Certain factors, which can be evaluated only after experience, have to be considered, and the practical approach is essential. The selection of a safety factor depends on the reliability of design data used, a careful consideration of service conditions, the reliability of underlying theory of design, and the consequences associated with failure. Safety factors between 1·125 and 2·00 are generally sufficient. The theory should include the effect of co-axial and hoop stresses; tension always reduces the collapse strength of a string.

Tables and diagrams illustrate stress distribution. A. J. H.

1287. A review of casing string design, principles, and practice. Pt II. J. O. Hills. *World Oil*, Oct. 1951, **133** (5), 141.—Concluding the article, there are presented data in graphical form facilitating the design of casing strings, even of the more complex forms, and enabling a rapid check to be made on the final design. The charts, which are fully explained, are taken from information booklets published by a manufacturing company. References. A. J. H.

1288. Abuses of wire ropes. C. M. Zerr. *World Oil*, June 1951, **132** (7), 114.—The majority of abuses to which wire rope is subjected is found in cable-tool drilling, which takes about 3% of the wire rope used in the U.S.A. Abuses common also to rotary drilling are considered, and illustrations given. The divisions under which rope abuse is considered are : handling and shipping, installation and rig use.

A. J. H.

1289. New fishing techniques for wire line devices. R. R. Rieke. *World Oil*, 1.7.51, **133** (1), 132.—Previously, fishing for wire line and electric surveying equipment has involved the running of drill pipe holding a fishing tool alongside the wire. In this method, however, by means of mechanical devices illustrated and explained, the wire line is cut and fitted with a spear head. With the use of an overshot and C-washer the drill pipe may then be connected with the wire line taut. Withdrawal is similarly

conducted. This system has proved effective and reduces the hazards involved in cutting a wire line or electric cable. A. J. H.

1290. Mud-logging. E. Vellinger. *Rev. Inst. franç Pétrole*, 1951, **6** (12), 399–402.—Interchange of fluids occurs between the formation and the mud, and if the mud circulation can be linked with the position of the bit, the point of interchange can be determined. Thus the points of ingress of gas, oil, or water can be fixed. Automatic equipment will extract gaseous hydrocarbons from mud, identify them, and record their amount. It is more difficult to deal with the oil, but logging is still possible. The logs so obtained reduce the need for mechanical coring.

If on circulating without drilling hydrocarbons continue to be present in the mud it may be decided to take a core.

According to Pixler, in a Gulf Coast area the amount of coring was halved after introducing mud logging. In difficult cases mud logging helps in interpreting electric logs. Usually there are advantages in recording methane and the higher homologues simultaneously. Horizons which do not give methane are poor or unproductive, even though the higher hydrocarbons are recorded. G. D. H.

1291. Quantitative log interpretation of the San Andres Dolomite. C. B. Scotty. *World Oil*, 1.7.51, **133** (1), 166.—Two wells in different W. Texas fields which penetrated the San Andres Dolomite were drilled to above the prospective producing formation. Coring was then commenced using oil as the circulating fluid, to facilitate the determination of fluid content from core samples; core recoveries were in the region of 95 and 96%. Following core analysis, the distributions were compared with resistivity, self-potential and γ-ray data, and neutron logs. These data were shown graphically.

It is concluded that the S.P. (self-potential) curve may be used as a locator for the shaly zones, while the neutron log enables the estimation of the porosity. The apparent resistivities did not show good agreement, but the accepted method of obtaining " true " resistivity enabled the resistivites to be well correlated. References.
A. J. H.

1292. The shielded electrode method. H. Guyod. *World Oil*, Dec. 1951, **133** (7), 134.—The original short-electrode method of logging has gradually evolved into, primarily, the long electrode, and subsequently the shielded—or guard—electrode, which consists of a short central electrode, above and below which are the shielding electrodes; the length of the shielding electrodes determine the formation of the current nappes, the current sheet being horizontal for a shield length/electrode dia ratio of infinity. In the analysis it is assumed that the general case of central electrode height to dia ratio being three be taken. The ratio shield length/electrode dia seldom exceeds about 7·5 : 1 or 8 : 1; this results in an overall length of approx 6 ft. The electrode locates with relative ease any thin beds which have thicknesses several times the height of the electrode. With beds thinner than this height the resultant log is an average " silhouette " of the formation.

The effect of mud is also considered. The formation resistivity may be accurately determined when the hole size is known, and no mud invasion takes place. If the hole size is unknown, the logs are more accurate with high-resistivity beds. Mud invasion does tend to " cloud " the logs.

The treatment is mathematical, and is illustrated diagrammatically and graphically. References. A. J. H.

1293. Interpretation of neutron well logs. W. L. Russel. *Bull. Amer. Ass. Petrol. Geol.*, 1952, **36** (2), 312.—The method of logging oil wells by the use of γ-ray and neutron logs is now standard practice in the U.S. and many other parts of the world, and the author summarizes the recent improvements that have been made in this important technique and the technical factors involved.

The effects of unusual conditions and the exceptions to the general rules of interpretation are also dealt with. Other topics described in the paper are the accuracy, errors, and limitations of natural γ-ray and neutron well logs, their uses and advantages, and the problems on which further research is needed. E. N. T.

1294. Simultaneous radiation logging in Kansas. V. J. Mercier. *World Oil*, Nov. 1951, **133** (6), 146.—Although in certain fields the running of separate γ-ray or neutron logs is sufficient, in the Kansas Area it was found necessary to run a log combining the above two and a casing collar log. These are described independently; the main difference between the formation logs is that the γ-ray log is a measure of the natural radioactivity of the formation, whereas the neutron log is a result of induced radiation. The casing collar log may be of the magnetic type, where contact with the casing is necessary, or of the induction type. The obvious benefit from simultaneous logging is the saving in rig time. A. J. H.

1295. Log analyser simplifies electric log quantitative calculations. R. G. Hamilton. *World Oil*, Aug. 1951, **133** (3), 143.—For the rapid evaluation of electric log data, a slide rule has been designed; it permits the determination of porosity, permeability, and water saturation by the Tixier method, and porosity and water saturation by the Archie method. Full description of manipulation. References. A. J. H.

1296. Porosity-profile determination from electric logs. T. R. Wright and S. J. Pirson. *Bull. Amer. Ass. Petrol. Geol.*, 1952, **36** (2), 299.—Some limitations of the method are described, and a number of practical illustrations are given.

Narrow-spaced resistivity-measuring systems used in electric logging of wells respond mostly to the resistivities of the mud in the well bore and that of the mud-filtrate-invaded zone. After the necessary corrections are made for hole size, electrode spacing, and mud resistivity, the true resistivity of the invaded zone is obtained. The latter is a function of mud resistivity and of its characteristics, as well as of the porosity of the formation and of other lithological factors such as the cementation and saturation exponents. These exponent values are reasonably characteristic of well-defined reservoir rocks. If reasonable assumptions are made on the resistivity of connate water, on the degree of its flushing by mud-filtrate invasion, and on residual oil and/or gas, porosity may be calculated at various levels in the well bore. E. N. T.

1297. Appraisal of drilling mud costs. Pt I. V. V. Horner. *World Oil*, Dec. 1951, **133** (7), 127.—Small changes in requirements of mud characteristics may lead to appreciable increase in general drilling cost. In the method of analysis described, the costs are divided into: final mud volume cost, miscellaneous cost, and maintenance cost. Each section of the analysis is illustrated by an example. A. J. H.

1298. The effect of mud filtrates and mud particles upon the permeabilities of cores. T. J. Nowak and R. F. Krueger. *World Oil*, 1.7.51, **133** (1), 125. (1951 *Spring mtng Pacific Coast, Divn of Production, API, Los Angeles.*)—It has been recognized that the permeability determinations on cores depend on the mud filtrate, and on the fluid used in the determination. This is particularly important with cores having clay content; swelling is more pronounced with certain aqueous solutions. Successive determinations were made with oil and synthesized formation waters to verify whether, or not, the original oil permeability could be re-established. The results, which are not well defined, show that the sequence of tests does fix largely the extent of the recovery of the original permeability. A. J. H.

1299. The effect of mud filtrates and mud particles upon the permeabilities of cores. Pt II. T. J. Nowak and R. F. Krueger. *World Oil*, Aug. 1951, **133** (3), 152.—In this concluding article the effect of mud particles is investigated. Well conditions are simulated by subjecting the cores, mounted in parallel, to pressure differentials of up to 1000 p.s.i. with mud at an average temp of about 175° F. Alundum cores were used to remove effects of clay swelling, common to some natural cores. The mud was jetted on to the cores, mounted in plastic, and continually scraped off, by means of a reciprocator. If conditions similar to those in the region on the hole away from the bit are required, then jetting is maintained, with the reciprocator fixed. Pipettes were used to measure the fluid flowed through the cores; it was observed that the discoloration increased with increase in permeability of the core, and cores of low permeability showed less filtration loss than those of higher permeability. Oil-base muds were also used.

The above observations are discussed, and alternative explanations put forward.

In view of the limited extent of the work, definite theories cannot be introduced. Conclusions relating to the two sections of the paper, dealing with mud filtrates and particles, are given. Diagrams, photographs, and references. A. J. H.

1300. Stability of muds in high temperature holes shown by surface tests. G. R. Gray, A. C. Cramer, and K. K. Litman. *World Oil*, Aug. 1951, **133** (3), 149.—Recent evidence has shown that muds circulating in deep wells, 12,000 to 15,000 ft, are subjected to temp much in excess of those at which normal tests are made. For the estimation of mud characteristics at these elevated temperatures, 250° to 300° F simple tests are described; the mud is contained in small sealed cells and subjected to oven conditions over a period of 24 hr. Three conditions are illustrated: untreated mud which set hard, yet retained the normal water content; mud, partially treated, which exhibited plastic properties; and suitably treated mud, which had the required characteristics for drilling. A. J. H.

1301. Gas replaces drilling mud in San Juan Basin operations. G. M. Wilson. *World Oil*, Aug. 1951, **133** (3), 128.—In certain regions the use of air as drilling medium has been practised, but the operations in the San Juan Basin are claimed to be the first successful operations using natural gas at a drilling depth of about 5000 ft. Advantages include: a marked increase in drilling rate from 150 to 200 ft/day by conventional methods, to averages of ½ to 1 ft/min with gas; an estimated bit penetration life of 300 to 400 ft, as opposed to 80 ft; the drilling of porous formations without fear of contamination by mud or lost circulation materials.

It is admitted that time will be required to develop more fully such a method, but the routine adopted is explained. Such problems relating to bit wear and lubrication, both of which were improved with the gas technique, erosion of equipment, which is small, and the collection of samples are dealt with. Owing to the higher gas rate of flow, samples collected at the surface bear more marked relation to the depth at which drilling is proceeding at the moment of collection. The cuttings emerge, for the greater part, in powder form. A. J. H.

1302. Unitized flow line aids rigging-up and handling of drilling fluid. W. B. Colvin. *World Oil*, June 1951, **132** (7), 119.—Description is given of a portable dual system for the continuous treatment of drilling fluid; the mud may be diverted without interrupting the delivery from the well. Transportation as two units is effected by dismantling the flanged connexions between the gathering box and shale pit. The speed of assembling justifies the initial expense. A. J. H.

1303. Unitized mud pumps increase flexibility. A. W. Shaw. *World Oil*, 1.7.51, **133** (1), 107.—The secondary rating of steam tools has been attributed principally to the lag in the design of unitized steam tools. It has been frequently stated that the steam tool will not survive, and initial expense of this nature is unjustified on these grounds; generally this criticism is unfounded and may be attributed to the lack of design.

Certain unitized rigs have been assembled to give flexible operation, in a period 80% lower than that required for normal steam-tools assembly. Constructional details and designs are explained with references to a lay-out sketch and photographs. Certain improvements, such as the continuous lubrication of pump rods, are included. A. J. H.

1304. Investigation of torque converter drives on mud pumps. D. F. Toomey and E. G. Chilton. *World Oil*, Sept. 1951, **133** (4), 189. (*Spring Mtng Pacific Coast, Div'n of Production, API., Los Angeles.*)—With the introduction of torque converters power slush pumps are proving to be as well suited to conditions as the more conventional steam-driven pump. The latter was found to adapt itself to flow conditions, while the former tended to labour in an effort to adjust the conditions. The torque converters have reduced the pressure fluctuations by as much as 50%. In general, slower pumping speeds are advantageous. References. A. J. H.

1305. Rotary percussion drilling in West Texas. J. A. Wanamaker. *World Oil*, Sept. 1951, **133** (4), 182.—Rotary percussion drilling was patented some sixty years

ago, but only since 1948 have major developments taken place. Principal difficulties consisted of bit failure, but bits have been developed, and are being developed, for various types of formation. The solid journal bearings are maintained in design to give added strength in the percussive action. Constructional features are given, and examples quoted of successful operations. A. J. H.

1306. Wet auger drilling of seismograph shot holes. J. M. Camp. *World Oil*, Nov. 1951, **133** (6), 138.—The use of conventional shot-hole drilling equipment requires 100 to 300 gal water/100 ft of hole penetrated. This particular system can operate efficiently on 20 to 25 gal/100 ft. Its light construction permits easier transportation. A. J. H.

1307. Strata variants create reactions in plugged wells. F. R. Cozzens. *World Oil*, Dec. 1951, **133** (7), 151.—Imperfectly plugged holes may later provide many hazards due to leakage and formation of abnormally high-pressure zones in certain areas. The process is, in fact, quite exacting. Points to be considered include the initial cleaning of the hole, the use of different plugs, their location and method of fixing, and length of backing cement plug. A. J. H.

1308. Rowan's barge rig 13. J. A. Boatman. *World Oil*, Nov. 1951, **133** (6), 119.—An illustrated and detailed description of the barge rig used in Timbalier Bay, Louisiana. The equipment requirements and limited space do not permit anything but a compact design. The barge derrick is rated at 800,000 lb, and wind load capacity of 135 m.p.h. Although the original derrick was 154 by 30 ft, the construction would permit the installation of a rig 187 by 38 ft. A. J. H.

1309. Patents. U.S.P. 2,573,959 (24.2.48; 6.11.51). P. W. Fischer, assr to Union Oil Co. of California. Drilling fluid comprising 40 to 90 wt-% mineral oil, 0·05 to 10 wt-% water, 0·1 to 10 wt-% oil-dispersible metal soap, 0·01 to 5 wt-% water-sol salt *A* of a strong base and a weak inorganic acid, forming an oil-external emulsion to which *A* imparts gel-strength properties.

U.S.P. 2,573,960 (22.4.49; 6.11.51). P. W. Fischer, assr to Union Oil Co. of California. Drilling fluid comprising 50 to 75 wt-% heavy metal or alkaline-earth metal resinates or naphthenates, 10 to 25 wt-%hydratable clay and sufficient of a $>C_6$ glycol to give fluidity.

U.S.P. 2,573,961 (5.6.50; 6.11.51). P. W. Fischer, assr to Union Oil Co. of California. Drilling fluid of low electrical resistivity is prepared by dispersing in mineral oil 0·1 to 5 wt-% hydratable clay, 1 to 10 wt-% saponified rosin product *A* containing 1 to 15 wt-% free resin acids, an alkaline-earth metal base *B* (60 to 80% equivalent of *A*), and water to give a final content of 1·5 to 5 wt-%, allowing *A* and *B* to react and then adding alkali-metal silicate to give a final content of 0·3 to 0·6 wt-%.

U.S.P. 2,573,690 (25.3.48; 6.11.51). P. H. Cardwell and P. D. Muir, assrs to Dow Chemical Co. A fluid-permeable earth formation penetrated by a well bore is consolidated by introducing a liquid mixture of a phenol, an aldehyde, and a polymerization catalyst, capable of forming a hard resin. V. P. P.

Production

1310. A review of reservoir engineering. Pt 2. N. J. Clark. *World Oil*, June 1951, **132** (7), 184.—A simplified approach to the description of various reservoirs with diagrammatic illustrations. References. A. J. H.

1311. Relaxation methods applied to oilfield research. H. Dykstra and R. L. Parsons. *Petrol. Tech.*, **3** (8), Aug. 1951, *AIMME Tech. Paper No.* 3145, 227–32.—The application of the " relaxation " techniques to problems of steady state fluid flow is demonstrated. In order to obtain the pressure distribution the steps are as follows : 1. Draw on a large scale the region under study and cover it with a coarse square grid. 2. Put on the known pressures, and sketch equipotential lines as accurately as possible and guess the pressures at the grid points. 3. Determine the relaxation equations and

calculate the residual at each grid point. 4. Relax the residuals, starting with the largest. In general, when a change of one-half makes the surrounding residuals larger, the residuals have reached a practical min. 5. When a residual is surrounded by residuals of the same sign, make the correction large enough to change the residual's sign while leaving its magnitude about the same. This procedure causes the solution to be attained more rapidly. 6. For greater precision apply a finer net as the next step.

The solutions are particular, not general, but are often reached more quickly than by analytical methods, while the technique is applicable to almost any problem.

G. D. H.

1312. Variation of oil characteristics with elevation in oil reservoirs. C. Q. Cupps, P. H. Lipstate, and J. Fry. *World Oil*, Dec. 1951, **133** (7), 192.—Recent investigations made under the U.S. Bureau of Mines in the Weber reservoir, Rangely field, Colorado, over a period of three years would indicate that the composition of a crude varies greatly with depth. With the limited available data, it is impossible to define closely the conclusions, but the degree of variation in the reservoir would suggest that the reservoir fluid was not in fact uniform; this is deduced from present concepts of equilibria in petroleum reservoirs. Certain authorities have maintained that over geologic time, equilibrium in a reservoir must be reached, and that variation in fluid characteristics is brought about only by leakage from the reservoir, or penetration into the dome by producing wells. It has also been stated that a progressive variation in composition would be obtained in a system under gravitational field. This theory does agree more closely with the findings in the Rangely field. The practical interest is that sampling should be carried over a larger section of a reservoir before assigning definite characteristics to it.

A. J. H.

1313. Reservoir fluids and their behaviour. D. L. Katz and B. Williams. *Bull. Amer. Ass. Petrol. Geol.*, 1952, **36** (2), 342.—As drilling for oil becomes progressively deeper it is important to review the likely changes in properties of the oil and gas phases of reservoir fluids found at increasing depths.

The phase changes which take place for the fluids which remain in the reservoir during the pressure reduction normally accompanying production and for the fluids produced from the wells through separators at the surface are of interest to those concerned with recovering oil and gas. This paper describes the behaviour of oil and gas mixtures in the reservoir and as produced at the surface. The significance of this behaviour in oil and gas production is discussed. The possibility of applying the knowledge of phase behaviour to develop procedures for recovering crude oil from deep gas-drive fields is included.

E. N. T.

1314. The Benton water flood, Franklin County, Ill. C. V. Cameron. *Petrol. Tech.*, Sept. 1951, **3** (9), 9–13.—Benton is an anticlinal structure with 70 ft of closure in the field. Production is from the Tar Springs, which change to shale to the north and to the south. There was no original gas cap, and from 1941 to 1949 the behaviour was almost a text-book example of depletion-type performance, but there was some indication of water advance from the west. When water injection began the cumulative production was 20,200,000 brl, and the primary recovery was expected to be 26 to 27 million barrels.

Because of mining operations high injection pressures were not possible, and a 20-acre five-spot pattern was adopted to limit infill drilling. 90% of the area was unitized, and eighty-four wells were converted for injection by cleaning, plugging back, or deepening. 120 wells were used for production. Water was piped from Lake Moses and treated together with produced water in a plant capable of 30,000 b.d.

Before beginning injection the production was 1400 b.d. of oil and 550 b.d. water. Conversion of producers to injection wells changed the rates to 730 b.d. of oil and 255 b.d. water. After thirteen months of water injection the rate was 3250 b.d. of oil and 1670 b.d. water. About a third of the injection wells had pressures exceeding 500 p.s.i.

The theoretical additional recovery due to flooding is estimated as 28,300,000 brl.

G. D. H.

1315. Winter operations in Western Canada. G. D. Wright. *World Oil*, Dec. 1951, **133** (7), 169. (*Western Mtng, Canadian Inst. of Min & Metall*, Oct. 3–5, 1951, *Calgary, Alberta.*)—Problems encountered in field operations range from the housing of pumping

and producing units, much reduced efficiencies of units, and also personnel, the limited temp range of certain lubricants, the effect of cold on metals. At present operators have to modify plant initially designed for warmer climates. A. J. H.

1316. Completion practices in the Spraberry. H. E. Legendre. *World Oil*, Sept. 1951, **133** (4), 230.—A general review of methods adopted in the recently discovered field, where completion practices play such an important part, determining whether a well is to be a flowing well, a pumper, or even quite dry. A. J. H.

1317. The full hole gravel pack. A new completion technique. R. L. O'Shields and M. F. Hawkins. *World Oil*, Aug. 1951, **133** (3), 185.—Gravel packing in fields with sanding problems has largely been unsuccessful. In the laboratory study explanation is given of some of the factors which contribute to the failure of this form of completion. In the new technique no liner is set, and although productivity is slightly reduced, this reduction is negligible. The use of the finer gravels, not larger than 0·060 to 0·090 inch, is recommended, and to prevent sand blocking the perforations the gravel should be forced outside the casing.

The experimental and practical aspects are fully explained with diagrams and data. A. J. H.

1318. Hydrates in the natural gas industry. J.-P. Lacroix. *Rev. Inst. franç. Pétrole*, 1952, **7** (2), 34–49.—The formation of gas hydrates has long been known, and the existence of natural-gas hydrates is of practical significance, since they may obstruct pipelines. The apparatus and techniques for laboratory studies of hydrate formation are described, and curves present data for the hydrates of methane, ethane, *n*-butane, and propane. Hydrates of higher hydrocarbons are not known. It appears that many of the hydrates may have 6 or 7 molecules of water.

Tables give thermodynamic data for the various hydrates.

The conditions for the formation of natural-gas hydrates are discussed. Turbulence or factors leading to it favour their formation. Katz and his co-workers are almost convinced that hydrocarbon hydrates form solid solutions. Data are given on the modification of the conditions of equilibrium of methane hydrate when ethane, butane, or propane are present.

The lowering of the temp of hydrate formation by the addition of inhibitors has been studied. Amongst the most active compounds are ammonia and methanol. Their activity is a function of their concentration.

(Article is a résumé of the literature on natural-gas hydrates.) G. D. H.

1319. Relative merits of test procedures for natural gas wells. C. H. Hinton. *World Oil*, Oct. 1951, **133** (5), 176.—The development of the natural-gas industry has required that the old system of pilot-tube well testing be replaced by the more economical back-pressure open-flow method. The main error lies in the inaccuracies of the friction factor formulæ, and some authorities are adopting the Cullender and Binckley factor in preference to the Weymouth factor. Various test procedures are described. A. J. H.

1320. Pure Oil's Rollover field has first offshore gas condensate production. G. R. Olsen. *World Oil*, Oct. 1951, **133** (5), 169.—In the production of condensate, over 8 miles from the Louisiana coast and in water of approx 40 ft depth, the complications are two-fold, arising from offshore operations and condensate problems. The main features include: shut-in pressure of 3000 p.s.i., with injection pressure of 1200 p.s.i. into the submarine line linking the unit to the shore-tank battery; the processing of gas to remove water, preferably to a concentration of 7 lb/million cu. ft. gas, and not to exceed 14 lb/million cu. ft., to prevent the plugging of the line by hydrates; the min sizes of equipment, since four wells are produced from the same offshore platform; safety devices to shut in wells under adverse conditions. The operations are fully described. Diagrams and photographs. A. J. H.

1321. Heat losses from buried gas gathering lines. J. T. Simon. *World Oil*, Nov. 1951, **133** (6), 171.—For gas transmission along long pipelines, the only satisfactory method for prevention of hydrates is the removal of the water. In some instances,

however, the removal of water along short lines is impractical, and the pressure–temp characteristics of the hydrates should be considered; the principle is to maintain the line temp above the range in which hydrates are formed. To this end, heaters along the short lines may be installed. By direct equation of heat transmission from the line to surroundings and heat supplied to the gas, the required temp and heating capacity are estimated. The heat loss coefficient has to be selected for the particular conditions. Consideration of typical field problems is given, and practical points mentioned. A. J. H.

1322. Gas gathering facilities of the Snyder gasoline plant. H. G. Teverbaugh. *World Oil*, Sept. 1951, **133** (4), 275.—Design features of a gas-gathering project, which has enabled the conservation of 4 (U.S.) billion cu. ft. of gas during the first year of operation. The project embraces separate high-pressure and low-pressure gathering systems. Diagrams. A. J. H.

1323. Gas lift practices in West Texas. J. R. Hamilton. *World Oil*, Sept. 1951, **133** (4), 250.—A general review, with reference to problems specific to certain fields. Two main groups exist: continuous gas lift, and "slug lifting." A. J. H.

1324. Calculation of natural condensate recovery. T. W. Brinkley and R. C. Curtis. *World Oil*, June 1951, **132** (7), 178.—The cost of installing equipment for the maintenance of pressure in condensate reservoirs requires that preliminary estimate of the recovery be made. Two methods are outlined: the correlation of reservoir volume factors and recovery percentages with gas/condensate ratio; the calculation of incremental gas production per unit pressure drop, and the condensate recovery per unit volume of gas production, to give the condensate production per unit pressure drop, and the subsequent summation of the increments. The second method is based on sample data.

The theory is supplemented by sample data and calculations. Two references. A. J. H.

1325. Pressure maintenance in Block 31 field. R. C. Hartman. *World Oil*, Sept. 1951, **133** (4), 223.—Operational features in Crane County, Texas, in which 9 million cu. ft/day of stripped gas are re-injected at a pressure of about 4100 p.s.i. The operators of the field have combined in an effort to maintain the high original reservoir pressure. A. J. H.

1326. Calculation of the bottom-hole pressure of a gas well. J.-P. Lacroix. *Rev. Inst. franç. Pétrole*, Feb. 1952, **7** (2), 27–31.—In using Weymouth's formula to calculate the bottom-hole pressure of a flow gas well, the result was found not to agree with that measured with an Amerada bottom-hole pressure gauge. This is not unexpected, since the formula is for horizontal flow and for Reynold's numbers of the order of 1,000,000.

A formula has been derived for flow in a well assuming the flow to be isothermal and at the mean temp of the column, and to be uniform, and the gas to be homogeneous, and is as follows:—

$$Q = 0{\cdot}94955\,\frac{1}{ZT}\sqrt{\frac{1}{f}}\sqrt{\frac{d^5(P_f^2 - e^s P_s^2)}{e^s - 1}}$$

where d = dia of column in mm, f = friction factor, T = mean absolute temp of gas, Z = mean coefficient of compressibility of gas, $e = 2{\cdot}71828$, Q = output in m³/day under standard conditions, $s = \dfrac{2Zg}{ZTb}$ and must be obtained by successive approximations, l = length of column in cm, g = acceleration due to gravity, b = perfect gas constant for 1 gm of gas in C.G.S. units, P_f = bottom-hole pressure in kg/cm², and P_s = top-hole surface pressure in kg/cm².

An average friction factor has been calculated from twenty-four tests made at Saint Marcet with flows of 1 to 14 × 10⁶ cu. ft/day at depths of 4900 to 6200 ft in 2½ E.U. tubing, and $\dfrac{1}{f} = 19{\cdot}8$, the range being 10·9 to 46·9; 18 of the figures ranged 16 to 24. G. D. H.

1327. Testing wells by back pressure method. G. W. Hereford. *World Oil*, June 1951, **132** (7), 198.—In normal gas wells it was found that the rate of production could be related to the pressures existing by the equation :—

$$Q = C(P_f^2 - P_s^2)^n$$

where Q = production in M.c.f/24 hr, C = a co-efficient, P_f = formation pressure, p.s.i.a., P_s = sand face pressure, p.s.i.a., n = an exponent. Allowing time for equilibrium, the gas is produced for various well-head pressures, commencing at complete shut-off conditions ; the results are plotted on log paper for the determination of the various constants.

The method is explained in stages, the necessary corrections being considered for head of flowing gas, etc, as set out by the Bureau of Mines procedure, and an example taken. Certain errors are particularly to be avoided ; they may give rise to appreciable misunderstanding. A. J. H.

1328. Surface indicating pressure, temperature, and flow equipment. M. B. Riordan. *Petrol. Tech.*, Sept. 1951, **3** (9), *AIMME Tech. Paper No.* 3080, 257–62.—When there are multiple sands of varying characteristics it is desirable to know what each is contributing at a given back-pressure. The equipment for measuring pressure, temp, and flow is run through a lubricator gland which is designed for pressures up to 3000 p.s.i. The flowmeter is of the turbine-impeller type, and drives a commutator through a magnetic coupling. The commutator interrupts a light beam generating a frequency signal via a photo-electric cell. An expansible packer can be made to contact the liner wall, thereby causing a max of fluid to pass through the meter.

Both temp and pressure measurements employ a device which utilizes the fact that the natural frequency of transverse vibrations of a stretched wire is proportional to the applied tension in the wire. When the vibration takes place in a magnetic field a variable frequency signal is generated. The temp element varies the wire tension by change in size of the frame supporting the frame ; the pressure element involves a diaphragm, and supporting the wire on a frame of the same material as the wire.

The surface equipment includes a comparator unit, oscilloscope, and power supply. A null-beat system permits visual matching of surface and subsurface frequencies to a fraction of a cycle.

Time in the well is unrestricted because no clocks or batteries are used. The usual procedure is to lower the device to just above the upper perforations and make a temp traverse, because any flow in an oil well has an associated temp effect. Any observed anomalies are carefully checked and bracketed, and then confirmed by pressure and flow traverses. Well conditions can be adjusted if required to obtain more information.

Gas entry is shown by a reversal or at least a diminution of the temperature gradient. Water entry is revealed by an increased temperature gradient.

Temp surveys in high G.O.R. flowing wells tubed to bottom can reveal points of main gas entry. G. D. H.

1329. 25 per cent more oil through pressure maintenance. J. A. Kornfeld. *Oil Gas J.*, 4.2.52, **50** (39), 62.—It is estimated that more than 25% over the primary oil production will be obtained by full-scale gas injection into a 6600-ft deep Pennsylvanian sand bar in Northeast Elmore field, Garvin County, Oklahoma. The field has 111 wells, covers an area of 3320 acres, and has a production of 3465 b.d. 19,000 M.c.f/day of gas is returned to the reservoir to assist the primary gas-cap drive. J. C. M. T.

1330. Measurement and use of relative permeability data. U. S. Branson. *World Oil*, 1.7.51, **133** (1), 184. (*Petroleum Branch, AIME, New Orleans, October*, 1950.)—Relative permeability is of great importance in the consideration of production problems, being one of the factors leading to a decline in production. The practical requirement in the field is the limit of production ; calculations of Productivity Index are based on Darcy's Equation for radial flow, correcting for relative permeability. Saturations are estimated from the material balance equation. Routine analysis is outlined, and data expressed graphically. References. A. J. H.

1331. Relative permeability studies. J. Fatt and H. Dykstra. *Petrol. Tech.*, Sept. 1951, **3** (9), *AIMME Tech. Paper No.* 3078, 249–56.—An equation is derived giving the

relative water permeability of a rock as a function of water saturation, by assuming that the sample can be represented by a bundle of capillary tubes in which the fluid-path length varies with the saturation and is not the same as the bulk length. The relationship is

$$K_r = \frac{\int_0^s \frac{ds}{P_c^{2(1+b)}}}{\int_0^{100} \frac{ds}{P_c^{2(1+b)}}}$$

where b is a constant. Its value is assumed to be $\frac{1}{2}$. The integrals are derived by the capillary pressure curves by replotting saturation against $\frac{1}{P_c^2}$ instead of against P_c and finding the area under the curve. Comparison with measured relative permeabilities indicates that for some sands $b < \frac{1}{2}$ and for others $b > \frac{1}{2}$.

Equipment for the measurement of relative permeabilities is also described.

G. D. H.

1332. Theoretical note on linear absorption methods of determination of fluid saturation in porous media. L. B. Lipson. *Petrol. Tech.*, Aug. 1951, **3** (8), 19–20.—The fluid saturation in porous media has been determined by measuring the X-ray linear absorbing power of particular fluids in the media. There are, however, theoretical reasons for considering that the absorption *v.* saturation curve for a linear absorption method is not necessarily a single-valued function of the saturation, and such non-unique behaviour needs to be evaluated. The principle is illustrated for a simple case using combinations of two different dielectrics. The cases of three different simple distributions of the dielectrics are considered, and three markedly different relationships are obtained for the dielectric constant of the combination. It is therefore concluded that the calibration curve for absorption would be dependent on the porous media and on the mode of attaining a given saturation. The absorption relationship would show hysteresis comparable with the differences between imbibition and drainage in the saturation history. G. D. H.

1333. Application of electrical resistivity measurements to problem of fluid flow in porous media. M. R. J. Wyllie and M. B. Spangler. *Bull. Amer. Ass. Petrol. Geol.*, 1952, **36** (2), 359.—This paper has as its principal object a discussion of the application of electrical-resistivity measurements to the study of flow processes in porous media. It is particularly concerned with the natural consolidated porous media of especial interest to the petroleum industry. In particular, it seeks to show that suitable electrical measurements of the resistivity of porous media either partly or wholly saturated with a conducting fluid may be used to derive a parameter which renders the Kozeny equation for fluid flow through porous media applicable to both consolidated and unconsolidated porous media, to partially saturated porous media, and to certain anisotropic porous media.

It is noted that the principal difference between unconsolidated and consolidated porous media lies in the higher tortuosities applicable to the latter. By the preparation of thin sections and the use of a statistical method for determining surface areas it is shown that the Kozeny equation appears to give valid surface areas for consolidated porous media. Such measurements make possible an estimate of the average grain sizes of many consolidated porous media. E. N. T.

1334. Water injection in primary production pays off. W. H. Davis. *World Oil*, Dec. 1951, **133** (7), 187.—Essentially a report on water injection in primary stages of production from Patoka Rosiclare, Ill. Pressure maintenance by gas injection has been applied in the initial stages of production in several cases, but little attention had been paid to the use of water. Brine water, aerated and treated, was used for injection. Operating costs were much reduced owing to the relevant data being available from the early records. A contour map gives the location of injection and producing wells; the Patoka Rosiclare is of anticlinal structure of 20 ft max productive closure. Production was increased from 60 b.d. to a peak of 1040 b.d. following the commencement of water injection. A. J. H.

1335. Primary high pressure water flooding in the Pettit lime Haynesville field. D. W. Akins. *Petrol. Tech.*, Sept. 1951, **3** (9), *AIMME Tech. Paper No.* 3077, 239–48.—The Haynesville Pettit field, discovered in 1941, has 189 producing wells in 14,500 acres. The depth is about 5300 ft, and the unitized zone has two zones of porosity about 40 ft apart; the Upper Pettit zone is itself separated into two parts over most of the area by a thin shale. The porosity averages 19% and the permeability 23 mD. The closure is only 20 ft, but producing elevations range 500 ft. All wells were acidized to give production. There is no gas cap, and the saturation pressure was 2331 p.s.i., with 460 cu. ft/brl of dissolved gas. The field is bounded by low porosity and permeability. The average connate water content is 23%.

Return of gas began in Jan. 1945, when the producing G.O.R. was 2230 and the bottom-hole pressure 1400 p.s.i. The output was 340,000 brl/month, but dropped to 150,000 brl/month in Nov. 1945. The injection rate was 15·7 M.M.c.f/day, but this was raised to 22·5 M.M.c.f/day in Jan. 1946, and output was raised about 80,000 brl/month immediately. Although it was clear that some wells would probably never benefit during the economic life of the project, there were beneficial changes in G.O.R. and bottom-hole pressure trends.

A high G.O.R. well in the north was used for water injection starting in March 1946. This took 1100 b.d. at 1200 p.s.i. surface pressure. By July 4 wells were in use for water injection. Wells adjacent to the first injection well showed pressure rises, and in those producing the G.O.R. fell and oil output rose. A line drive was established so that wells in the north outside the sphere of influence of gas injection would benefit. By Sept. 1947 seventeen injection wells were in use and 2,874,997 brl of water had been injected. Most of the gas has been returned to the upper part of the upper Pettit, and most of the water to the lower part of the upper Pettit. Recovery efficiencies of 35% have been calculated for the Upper Pettit. To date 14·1% of the producible oil in the lower part may have been by-passed, but the ultimate recovery may be twice that expected by the original dissolved gas drive. G. D. H.

1336. Phase behaviour of a natural hydrocarbon system. C. F. Weinang and H. B. Bradley. *Petrol. Tech.*, Aug. 1951, **3** (8), *AIMME Tech. Paper No.* 3097, 233–8.—The hydrocarbon system was formed by recombining vapour and liquid samples from the first-stage separator of the well. The composition in mole per cent was CO_2 0·13, N_2 53·91, C_2H_6 14·2, C_3H_8 9·64, *iso*butane 1·25, *n*-butane 4·29 *iso*pentane 1·12, *n*-pentane 1·87, C_6H_{14} 2·72, heptanes (mol. wt. 178·50) 10·11.

The P.V.T. apparatus consisted mainly of a two-section, double-windowed gauge, mounted in a constant-temp air bath. The experimental data are tabulated at temps of 80·5°, 101·2°, 121·1°, 141°, 161°, 170·9°, 181°, 191·2°, 196·2°, 201·3°, 212·4°, and 226·4° F.

The system showed unusual behaviour only in the region below the critical temp. As the pressure of the system is increased normal condensation takes place with increase of liquid to a max, after which further increase of pressure causes a decrease in liquid to a min, followed by a large increase and eventual passage into a single-phase region through a bubble point. This behaviour is referred to as renascent vaporization or condensation.

Plots and cross-plots of the data are given. G. D. H.

1337. Phase equilibria in hydrocarbon–water systems. III. Solubility of methane in water at pressures to 10,000 p.s.i.a. O. L. Culberson. *Petrol. Tech.*, Aug. 1951, **3** (8), *AIMME Tech. Paper No.* 3082, 223–6.—Experimental data on the solubility of methane in water at 77°, 100°, 160°, 220°, 280°, and 340° F have been obtained at pressures up to 10,000 p.s.i.a. These data are presented in tabular and graphical form, with some smoothed values.

Comparisons are made with ethane–water and natural-gas–water systems. At low pressures the solubilities of ethane and methane are very nearly the same, but as the pressure increases the former becomes more soluble than the latter. G. D. H.

1338. Interpretation of chemical water analysis by means of patterns. H. A. Stiff. *Petrol. Tech.*, Oct. 1951, **3** (1), 15–16.—Horizontal lines extending right and left of the vertical zero line form the basis of the pattern. Positive ions are plotted to the left, negative ions to the right. The units are milli-equivalents per litre, the units for

sodium and chloride being ten times those for the other ions. The patterns are obtained by joining the plotted points for the several ions, and these may be characteristic in form or size. Dilution changes the size but not the general form. The pattern can be used for correlation.

Examples of the use of the patterns are given. G. D. H.

1339. Supply, sources and treatment of flood water. H. S. Barger. *World Oil*, Aug. 1951, **133** (3), 213.—Aspects of a water-flood project presented to enable the operator to study the particular problems. In every case water requirements should be considered with reference to losses within the reservoir. The treatment of the water depends primarily on the nature of the source of the water, and secondarily on the conditions within the sand body; it is imperative also to minimize corrosion of equipment. Certain lines for future research are mentioned. References. A. J. H.

1340. Deep zone flooding in Arkansas. S. S. Lacy. *World Oil*, Aug. 1951, **133** (3), 192.—A report on a unitized repressuring scheme for the recovery of the bottom-hole pressure of the Hogg sand in the Wesson field, Ouachita County, Arkansas. The system adopted proved successful, and up to May 1951 recovery was 25·1% of estimated ultimate recovery of 30,185,000 brl. A. J. H.

1341. Additional oil production through flooding with carbonated water. J. W. Martin. *World Oil*, Aug. 1951, **133** (3), 179. (*28th A.G.M., Penn Grade Crude Oil Assoc, Pittsburgh, June* 14, 1951.)—This form of recovery may more correctly be termed "chemical treatment." The principal factors affecting the recovery on a laboratory scale include: (i) the degree of carbonation of the flooding water—above 20 to 30% the relative advantage of carbonation increases more slowly; (ii) the oil-sand temp—higher temp promote recovery; (iii) the pressure of the sands—above about 500 p.s.i., the higher the pressure, the greater the recovery, but below this pressure, the effect is not marked; (iv) the nature of the crude; (v) natural-gas content, which increases the effect of flooding with carbonated water—with dead oil it is recommended that natural gas be injected. From the field tests it was observed also that the produced gas contained a greater percentage of unsaturated hydrocarbons. Corrosion was appreciably reduced. Possible explanations for the increased recovery, based principally on chemical behaviour, are given. A. J. H.

1342. Surface activity as applied to secondary petroleum production. F. D. Snell and C. T. Snell. *World Oil*, Nov. 1951, **133** (6), 184.—The principle of flushing sands with treated water consists in displacing the oil from the solid or sand grains, by preferentially wetting in the water phase. Of surface-active agents there exist three main groups, anion-active, cation-active, and non-ionic compounds. Although there is a large number of commercial products, they are derived from a limited number of such compounds. The phenomenon of wettability is discussed with reference to oil sands, and on a theoretical basis. It may be concluded that the desired characteristic of the agents should include: lowering of the contact angle made with the solid, the increase of interfacial tension between solution and crude oil, low emulsifying power, low reactivity with impurities in the sand, and also to an extent with the oil, and commercial cheapness.

The subject is dealt with fundamentally, and in detail; laboratory procedure is outlined. References. A. J. H.

1343. Removal of water and emulsion blocks to stimulate oil production. Pt I. W. F. Hower. *World Oil*, Oct. 1951, **133** (5), 195.—Some fundamental aspects of emulsions are discussed. Oilfield emulsions, such as found in a reservoir, may have been formed spontaneously, since the surface area in a sand is appreciably large. Although heating is a means of breaking emulsions, the formation pressure tends, however, to stabilize the emulsion, and the presence of certain clays also assists in the stabilization.

An aromatic sulphonic acid, marketed as "Morflo," has the required characteristics to break emulsions and increase the production from a sand; it is insoluble in oil, soluble in water, and reduces the surface tension of the latter. This fact is of particular importance, since it reduces the effectiveness of the bentonitic material as a stabilizer. A. J. H.

1344. Developments in the chemical treatment of wells in the Permian Basin. R. S. Ousterhout. *World Oil*, Sept. 1951, **133** (4), 236.—The principles involved have been applied particularly in the Permian Basin, but are equally suitable to formations which are susceptible to acid treatment. A new channelling acid has been developed with viscous properties (200 to 400 cp); and the ability to form a film over the surface of the formation, which film may then be dissolved into a non-viscous solution by hydrochloric acid. The viscous nature of the solution ensures that only the larger pores of the sand are entered, and so the formation is penetrated; this acid compound may penetrate ten or fifteen times farther than hydrochloric acid. Control of silicate swelling has also resulted in increased production rates. A. J. H.

1345. Value of agents to control silicate swelling in acidizing. P. H. Cardwell. *World Oil*, 1.7.51, **133** (1), 159. (*Spring Mtng, Mid-Continent District, API Divn of Production Amarillo, Texas.*)—Certain materials, insoluble in hydrochloric acid, have been found to reduce appreciably the effectiveness of an acidizing operation. Such clay minerals, of the montmorillonite–beidellite, kaolin, and illite groups, may actually swell during a treatment, depending on their location and reaction with the acid. The development of the investigation led to the use of certain silicate swelling control agents which have a three-fold application in the formation: the reduction of emulsion of the produced oil, the required increase in permeability, and the increased return on spent acid. The use of these control agents has been successfully demonstrated in certain wells.

An analysis is given of the reactions contributing to the behaviour of the clays, and is illustrated with reference to particular clays and formations. References. A. J. H.

1346. High temperature gauge glass for the visual observation of critical phenomena. J. R. Spencer. *Petrol. Tech.*, Aug. 1951, **3** (8), 17–19.—A detailed description is given of a capillary tube variable-volume cell for phase-relation studies of hydrocarbon systems. The apparatus has been used satisfactorily over the ranges 100° to 550° F and 1500 to 3500 p.s.i. The cell contents are entirely visible over 97% of the capillary. It has been possible to establish the critical conditions for a particular mixture in the course of a day's run. A disadvantage is the small amount of material available for subsequent analysis. G. D. H.

1347. Practical offshore production practices at Bay Marchand. J. E. Kastrop. *World Oil*, June 1951, **132** (7), 167.—Problems encountered in this region have to be considered with particular reference to the weather conditions.

Twenty-eight producing wells deliver to six main steel structures from which the oil is pumped ashore through three 4-inch submarine lines. Low tubing pressures and sanding problems have necessitated the installation of pumping units. Power for production and subsequent drilling is provided through submarine cables and is distributed from "D" structure through transformers and switches to other structures. Telephone lines, included in the submarine line, and two-way radio link up the shore and offshore installations. Safety measures, which form an essential part of such units, are described. A. J. H.

1348. New techniques for application of plastics in consolidating formations. H. B. Ritch and P. H. Cardwell. *World Oil*, Dec. 1951, **133** (7), 177.—The essential feature of consolidation of sands by plastics is the consolidation of the sand particles and the retention of permeability. The liquid volume of the injected plastic is greater than the volume of the solid, and is dependent on the nature of the sand. Thus finer sands require larger liquid volume/set volume ratio than do coarser. The latest techniques consist in cleaning the well and infiltered region by primary injection of a mud acid, a mixture which includes hydrofluoric and hydrochloric acids with suitable inhibitors, and in subsequent complete injection of the plastics into the sand. The original idea of allowing plastics to cover the perforations has been superseded by a system whereby the perforations are left clear. If subsequent plastic treatments have to be made for a satisfactory overall operation, then mud acid is not used.

Following a description of the method, some field results are given, and discussed. References. A. J. H.

Oilfield Development

1349. Our unproduced reserves; what are they? M. Muskat. *J. Inst. Petrol.*, 1951, **37**, 717–28.—The prediction of unproduced reserves should be related to the anticipated manner of field operation, because the magnitude of the oil recovery in any one field may be materially affected by the mode of field operation. The role which improved engineering practices can play in increasing the magnitude of recovery is reviewed, and some of the possible methods which may develop are indicated.
A. R. W. B.

1350. 1951 exploration established record. Anon. *World Oil*, 1.2.52, **134** (2), 81.—10,793 exploratory wells were completed in the U.S.A. in 1951, 2047 more than in the previous year. 1036 wells were completed in Dec. 1951.

1001 new oil fields were discovered in the U.S.A. during the year, compared with 816 in 1950.

Tables give the results of exploratory drilling in the U.S.A. in Dec. 1951 and twelve months, 1951–1950, by districts, and a summary of the results of exploratory drilling.
C. A. F.

1351. World oil production. Anon. *Petroleum*, Feb. 1952, **15** (2), 49.—World crude production and natural gasoline output for 1951 is estimated at over 600 million tons, approx 10% higher than the 1950 figure of 543 million tons. The U.S.A. produced more than 50% of the total, followed by Venezuela, the U.S.S.R., Saudi-Arabia, and Kuwait. C. A. F.

1352. 152 geophysical crews search Western Canada. Anon. *World Oil*, 1.2.52, **134** (2), 240.—152 geophysical crews were carrying out seismic, gravity, and magnetometer exploration in the states of Western Canada. A table gives, by companies, the number of seismic, gravity, magnetometer, and total field parties now operating. C. A. F.

1353. Seismic survey off coast of Trinidad is scheduled. Anon. *World Oil*, 1.2.52, **134** (2), 246.—A seismic survey is to be made this year in the Gulf of Paria off the coast of Trinidad to search for offshore structures. C. A. F.

1354. Yugoslavian exploration. Anon. *Petroleum*, Feb. 1952, **15** (2), 48.—Oil has been found in Yugoslavia in the Prekmusje, near Zagreb and in various districts of the Vojvordina, Dalmatia, and Montenegro.

Recent exploration indicates that deposits in Dalmatia are likely to be of major importance. C. A. F.

1355. Status of Russian petroleum industry. Anon. *Petrol. Engr*, Dec. 1951, **23** (13), B79.—According to Russian and foreign sources, total production of the U.S.S.R. in 1950 was 273,200,000 brl.

Oilfields in the Caucasus are slowly declining, and development of the "Second Baku" fields in the middle Volga Valley is increasing. 40 to 50% of 1950 production came from the "eastern fields" in the republics of Bashkir and Tatar, and the Kuibyshev territory. Development of fields offshore from Baku in the Caspian Sea has been started.

Refinery capacity has been enlarged, and new refineries are being constructed at Bensina and Potapovo in the Ufa area. Pipelines have also been extended. C. A. F.

1356. More Iraq oil. Anon. *Petroleum*, Mar. 1952, **15** (3), 57.—Test wells drilled in 1948 at Zubair, Nahr Umr, and Ratawi in southern Iraq found commercial oil in Cretaceous sands between 10,000 and 11,000 ft in these areas. Development has been concentrated at Zubair, where twelve wells have been drilled, and field installations, including storage tanks and a power-station, have been built. The first production from the field was loaded last year from Fao, the terminal, which is connected to the field by a 70-mile pipeline. Exports in 1951 are expected to be 2·2 million tons.
C. A. F.

1357. Kuwait. Pt 2. F. D. Potter. *World Oil*, 1.2.52, **134** (2), 232.—Drilling and completion practice and oilfield development in Kuwait at the head of the Persian Gulf are described.

Wells are drilled on 550-acre spacing and are completed as dual producers, each well producing from two of the three main Middle Cretaceous sands which are productive in the field. Min depth to the top of the First sand is 3600 ft, and max depth to oil–water level in the Fourth sand is 4800 ft. The Third and Fourth sands are the main producers, and are poorly cemented with low core recovery.

Crude from the wells flows through a 6-inch line to one of six gathering centres, where it passes through a seven-stage separation. Gas is flared and oil pumped to Ahmadi, where there is a storage battery of 168,000 brl capacity. From here there is a gravity flow to the coast terminal, where there are loading installations, a small refinery, power-stations, and other installations. C. A. F.

1358. First test well drilled Nigeria, West Africa. Anon. *Petrol. Engr*, Dec. 1951, **23** (13), B92.—A deep test is being drilled near Owerri in eastern Nigeria. Exploration in the area has been carried out since 1946, and approx three-quarters of the concession has been tested by seismic and gravity methods. C. A. F.

1359. Exploration underway in East and West Pakistan. Anon. *Petrol. Engr*, Jan. 1952, **24** (1), B92.—Core holes are being drilled northeast of Sylhet in Pakistan as part of an extensive campaign of exploration in eastern and western Pakistan. The work is estimated to take about six months, and a future deep test well is planned. C. A. F.

1360. Assamese test drilling. Anon. *Petroleum*, Feb. 1952, **15** (2), 29.—Deep drilling is to start in the Brahmaputra Valley, Assam, as a result of intensive exploration of 8000 sq. m. The site for the well is near Nahovkatiya in the northeast corner of the state. A well is being drilled at Nichuguard in the Naga Hills; it is dry to 3700 ft. C. A. F.

1361. Renewed oil exploration will begin in Australia. Anon. *World Oil*, 1.2.52, **134** (2), 240.—An area of approx 300,000 sq. m. in the Northwest Cape region of Western Australia is to be explored by a new company.

Geological and geophysical surveys in various parts of the country have been continued, and aerial magnetometer surveys are being made in the Lakes Entrance area in Victoria; similar surveys are planned elsewhere. C. A. F.

1362. Brief history of the search for oil in the Australian Commonwealth. A. Wade. *J. Inst. Petrol.*, 1951, **37**, 696–716.—Owing to the nature of the mining laws in Australia, until recently regional prospecting was unpracticable and large-scale operations were uneconomic. It is only within the past few years that any of the major oil companies have interested themselves in the search for oil in Australia. A brief chronological study of the search for oil in each Australian state and in Papua is given, and a list of references is quoted. A. R. W. B.

Transport and Storage

1363. Canadian pipeline expansion. B. Shiels and C. W. Smith. *World Oil*, Dec. 1951, **133** (7), 223.—The exceptional development of the Alberta crude and natural-gas production has resulted in a race for permits to build pipelines for the required distribution. The projected lines are discussed. A. J. H.

1364. Aspects of a trans-European oil pipeline system. Anon. *Erdöl u. Kohle*, 1952, **5**, 57–9.—Although in the U.S.A., total length of pipeline network (700,000 km) is about double that of the railways, Europe has no long-distance crude, petroleum products, or natural-gas pipelines. Western Europe is expected to be self-sufficient in refining capacity in the near future, main crude-oil source being the Middle East. This source of supply has been brought 4000 km nearer by the installation of TAP-line, which has made available 70 million tons of crude p.a. at the Levant coast. A similar project to by-pass the Iberian peninsula by means of a trans-European pipeline

is suggested. The main refining centres of Western (continental) Europe are situated in the Seine basin, at the Rhine-Schelde delta, lower Rhine Valley, and at the Weser and Elbe estuaries. Following pipeline route is suggested: from the Mediterranean port of Narbonne (S. France) to Bordeaux, thence via Orleans, Paris, Douai, Ghent, Antwerp, Emmerich, Bremen to Hamburg/Harburg. Suggested branch lines: Paris to Rouen, Douai to Dunkerque, Emmerich to Cologne. Approx total length, including branch lines, 2150 km; estimated capacity 20 million tons p.a.; dia of line decreasing from 70 to 23 cm according to distance from starting point; estimated total steel requirement 219,000 tons (including pumping-stations, intermediate storage, etc.); total cost $171 million; initial oil-input requirement 400,000 tons. Suggested route does not rise above 190 m above sea-level compared with 900 m for Tapline. Estimates are based on available figures for Tapline, and compare favourably with the latter in most respects, such as cost, saving in sea-tanker transport, and power expenditure. Great strategic value of project in war is noted. P. V.

1365. Pipeline flow efficiencies. C. McClure. *World Oil*, Sept. 1951, **133** (4), 282.—Where pipelines are of large dia, errors in flowing temp, gas gravity, and line pressure may lead to appreciable overall error in their design, and in the design of compressor stations. Gas flow has been estimated satisfactorily with a portable Pitot tube in the line; an accuracy of 2% is claimed.

Factors important in pigging a line are: detergent/water ratio, proper water-wall contact, pig velocity and type, and number of pigs used. The operations are described, with particular reference to practical data. A. J. H.

1366. Application of pipeline controls to field operations. H. T. Chilton. *Oil Gas J.*, 3.3.52, **50** (43), 85.—General application of field-control equipment, and two specific control-station installations in operation are discussed.

Starting and shut-down sequences of originating station and of a relay station are given, and protective controls described.

Economies to be effected in operating costs through use of control equipment in normally unattended station operation are also discussed. G. A. C.

1367. Selection of control valves for large capacity liquid pipelines. R. H. Putnam. *World Oil*, Oct. 1951, **133** (5), 230.—The elimination of pump surge tanks in pipeline systems, and replacement by a fully automatic closed system, contributes largely to saving costs in pumping power and to the conservation of the more volatile components of a crude. In an automatic system the requirement of a control valve is that it should give rise to little throttling in the normal open position, and yet, when necessary, should have well-defined throttling properties to control the flow. Stability of a valve is also important, and depends on the driving force operating against the unbalanced forces due to velocity changes.

Selection of valves is discussed with reference to valve-flow coefficients, and their behaviour under typical flow conditions. Graphical data. A. J. H.

1368. Cost and operating characteristics of microwave systems. E. B. Dunn. *World Oil*, June 1951, **132** (7), 223. (*Southern Gas Assoc., Biloxi, Miss, April* 23, 1951.)—Severe winter conditions have aroused interest in the use of these systems. The first micro-wave communication system was put into commercial operation in November 1949. Certain outstanding queries relating particularly to cost, manufacture, and dependability are answered. The paper refers mainly to pipeline communications. A. J. H.

1369. New type pressure storage tank. Anon. *Petrol. Process.*, 1952, **7** (1), 59.—The Horton Multisphere pressure storage tank is described with illustrations. The shell of the tank, which can be of unlimited size, is made up of a series of partial spheres. The intersecting edges of all the partial spheres are tied together internally with flat diaphragm plates, both horizontally and vertically. The largest yet built has a capacity of 2500 brl with a design pressure of 150 p.s.i. D. W. F.

1370. Collapsible storage tank. Anon. *World Oil*, June 1951, **132** (7), 236.—Principal difficulties in the use of collapsible tanks have been overcome in the "pillow" container of 10,000 gal capacity. The container is made of a synthetic rubber reinforced

with inner and outer layers of nylon cloth. Certain impregnations prevent porosity and serve as a barrier. The container may be packed up into a protective box, and easily unfolded. A. J. H.

1371. The expansion of vertical cylinders under liquid head. P. Kerr. *J. Inst. Petrol.*, 1951, **37**, 740–8.—The increase in capacity of a tank which occurs due to the outward pressure of the liquid contained therein, and the technical effects of this expansion, are discussed. A. R. W. B.

1372. Patents. B.P. 659,631 (1.3.49; 24.10.51). Thompson Bros. (Bilston) Ltd. and H. J. Thompson. Tanker road vehicle in which a large-capacity tank is supported near its rear end upon a semi-trailer and near its forward end upon the rear part of a tractor, the top of the tank being horizontal and the depth of the tank progressively increasing from front to rear so that the base of the tank is upwardly inclined towards the front end, thereby giving greater stability.

B.P. 657,909 (1.11.48; 26.9.51). Hammond Iron Works. Liquid storage tank is provided just above its horizontal median with an annular ring from which is hung a flexible diaphragm cover having a side wall and a bottom joined by flexible joint-covering devices forming a weighting means. At all positions of the diaphragm between empty and full the weighting means sinks into the surface of the liquid and defines an annular fold in the diaphragm, which, by flexure, varies in dia and in depth of immersion in the liquid with variations in the liquid level. V. P. P.

Refinery Operations

Refineries and Auxiliary Refinery Plant

1373. Modern refining processes. Anon. *Oil Gas J.*, 17.3.52, **50** (45), 188.—Flow sheets and descriptions of thirty-nine modern refining processes covering all types of feed stocks and products are given. G. A. C.

1374. Refineries go on stream in Western Europe. V. S. Swaminathan. *Petrol. Engr*, Feb. 1952, **24** (2), C5–8.—The new refineries at Pernis (Holland), Antwerp (Belgium), and Coryton (England) are described. Their respective capacities are 1¼ million, 1,320,000, and 850,000 tons/year of crude. E. K. J.

1375. Selection and operation of cooling towers. Anon. *Oil Gas J.*, 25.2.52, **50** (42), 181.—No. 111 in the refiner's notebook series presents a summary on cooling towers taken from papers contributed by the Power Division of ASME for a cooling-tower symposium. Performance factors, effect of closer approach, and checking of performance are dealt with. G. A. C.

1376. Selection and operation of water-cooling towers and air-cooled heat exchangers. H. E. Degler. *World Oil*, Dec. 1951, **133** (7), 228. (*Petroleum Mechanical Engng Conf., Tulsa*, Sept. 24–26, 1951.)—The more generally used form of water cooling is the cooling-tower method, but for certain conditions, particularly where the temp of the cooled fluid is higher, the dry-surface cooler is more economical. Careful consideration should be given to each type before the final selection. Development has followed upon the scarcity of water used in industrial processes. The operation and maintenance of the two types of cooling units are described with the aid of diagrams, and a brief outline given for estimating operating costs. A. J. H.

1377. Studies on fluidization. II—Heat transfer. C. van Heerden, P. Nobel, and D. W. van Krevelen. *Chem. Engng Sci.*, 1951, **1** (2), 51–66.—The second part of an experimental study on the characteristics of the fluidized state. This part gives an extensive investigation of the rate of heat transfer using a small-scale laboratory apparatus. The heat-transfer coefficient to the cylindrical wall of a fluidizing bed (" dense phase ") was measured under strongly varying conditions of gas and solids. The solids used were closely sized samples as well as mixtures of different sizes of

carborundum, iron oxide (Fe_3O_4), coke, lead, Devarda's alloy, and fly ash. The gases used were air, nitrogen–hydrogen mixtures, carbon dioxide, town's gas, and methane. For a correlation of the measuring results use is made of a system of dimensionless numbers that may be considered as a complete representation of all variables which may be expected to influence the value of the transfer coefficient. The gas rate is characterized by the reduced mass velocity G/G_0, where G_0 is the mass velocity where fluidization starts. A correlation based on this variable proves to be successful for Reynolds number <5, and can be written as

$$\frac{\mathrm{Nu}}{\mathrm{Pr}^{0.5}}\frac{1}{\phi'^{0.45}}\left(\frac{\rho_{bm}}{\rho}\right)^{0.18}\left(\frac{\rho C_p}{\rho_{bm}C_s}\right)^{0.36}=\psi(G/G_0)$$

Nu = Nusselt number, Pr = Prandtl number, $\phi'=\frac{\rho\rho_{bm}gd^3}{\mu^2}$ (dimensionless)

ρ, ρ_s = density of gas or of solid kg/m³;
ρ_{bm} = density of bed at maximal porosity;
Cp, C_s = specific heat of gas (at constant pressure) or of solid;
G/G_0 = reduced mass velocity (dimensionless);
G = mass velocity based on empty tube, kg/m² sec;
G_0 = critical mass velocity;

when $\psi(G/G_0)=0{\cdot}028\ (G/G_0)^{0.45}$ for $2<G/G_0<20$; a larger region ($1<G/G_0<30$) can be covered by $\psi(G/G_0)=0{\cdot}035\ (G/G_0-1)^{0.36}$

With the aid of the generalized shape factor B introduced in Pt I of this study, the above-mentioned relationship can be transformed into a correlation restricted to the region $2<G/G_0<20$. This can be written as:

$$\frac{\mathrm{Nu}}{\mathrm{Pr}^{0.5}}\left(\frac{\rho_{bm}}{\rho}\right)^{0.18}\left(\frac{\rho C_p}{\rho_{bm}C_s}\right)^{0.36}=\chi(B\ Re)$$

where for $Re<5$, $\chi\ (B\ Re)=0{\cdot}58\ (B\ Re)^{0.45}$ S. B.

1378. Heat transfer in the transition region in a tube under conditions of forced laminar flow. J. A. Businger. *Ingenieur*, 25.1.52, **64** (4), O.17.—This comparatively short paper points out how the heat transfer in the transition region reaches a max unaccompanied by any disproportionate rise in the flow resistance, and the economic importance of this fact is pointed out. The paper is illustrated by diagrams and mathematical derivations. R. R.

1379. Finned tubes find process uses. L. C. Johnston. *Chem. Engng*, 1952, **59** (1), 148–9.—Longitudinal fins silver-soldered or resistance-welded on to tubes find application where the individual film heat-transfer coefficients differ by more than 3 to 1. The extended surface reduces the temperature gradient in the film, and therefore reduces coking of residual oils and decomposition of heat-sensitive products.

Applications to tank heating and process work are described, and typical coefficients for nineteen pairs of fluids are given. D. H.

1380. Calculation of the efficiency of counter-current stage-wise mass transfer processes with constant distribution factor, when in the stationary state. I. Distribution of one component only. A. Klinkenberg. *Chem. Engng Sci.*, 1951, **1** (2), 86–93.—A rapid and easy method for the derivation of equations for counter-current, stage-wise, mass transfer of a single solute with a constant distribution factor, when in the stationary state is reported. The method is valid for a group of related processes, but is specifically applied to extraction in this case. Equations are derived for extraction with an intermediate feed point ("complete rectification") and for extraction with introduction of the feed at the end ("extraction" or "washing"). Some of their consequences are discussed. The use of reflux is included in the treatment, and also equations are given for the accumulation of solute in the feed stage. S. B.

1381. Calculation of the efficiency of counter-current stage-wise mass transfer processes with constant distribution factor, when in the stationary state. II. Stage requirements for the separation of two components by two solvent extractions. A. Klinkenberg, H. A. Lauiverier, and G. H. Reman. *Chem. Engng Sci.*, 1951, **1** (2), 93–9.—The

application of equations governing counter-current extraction as derived in Pt I, "Distribution of one component only" (Abs. 1380) to the two components of a binary mixture. Also methods are described to derive the min number of stages required for the separation of a given feed into products of a given composition. The results were applied to experiments reported by Schiebel. S. B.

1382. Estimating oil losses by atmospheric evaporation from refinery separator surfaces. P. S. Viles and C. T. Jones. *Refiner*, 1952, **31** (1), 117–19.—The evaporation of oils from plane surfaces has been studied, and an improved method is described for the estimation of losses from refinery tanks, separators, etc. A. R. H.

1383. Operation and maintenance of vertical gas driven compressors. J. B. Williams and V. E. Ford. *Refiner*, 1952, **31** (1), 99–102.—A routine of inspection for efficient operation and maintenance is presented. A. R. H.

1384. How to get what you need when your order compressors. D. P. Thornton. *Petrol. Process.*, 1951, **6** (12), 1365–9.—No. 6 in a series on how to order equipment. The principal specifications required with an order by compressor manufacturers are presented, together with common faults occurring in such specifications. D. W. F.

1385. How to maintain your pumps. H. F. Thompson. *Petrol. Process.*, 1952, **7** (1), 56–8.—The programme adopted at the Marcus Hook refinery of Sinclair Refining Co. to solve pump-maintenance and repair problems is described. A full-time pump inspector, whose duties include the handling and ordering of all spare parts, is responsible for checking pumping operations and for conducting three-monthly checks on all equipment for the purpose of carrying out preventive maintenance. D. W. F.

1386. Give mechanical seals a chance. D. R. Rankin. *Chem. Engng*, 1952, **59** (1), 152–3.—When changing from packed joints to mechanical seals difficulties are experienced in fitting and maintenance. Practical information is given to reduce these, to guide purchase, and to test new seals before installation. D. H.

1387. Mechanical seal retaining assemblies. L. T. Ellis, Jr., and C. L. Fussel. *Petrol. Engr*, Feb. 1952, **24** (2), C20–4.—Failure has occurred when mechanical seals have been used on pumps designed for soft packing. At one refinery 91% of the pump installations were found to be unsatisfactory due to weak bolting in 85% and weak glands in 25% of the pumps. Methods of re-designing weak-pump assemblies are given. E. K. J.

1388. The refiner's notebook. S. Chesler and B. W. Jesser. *Oil Gas J.*, 3.3.52, **50** (43), 95.—Pt 112 of this series describes relief valves, giving definitions and illustrating two conventional valves. A figure shows forces acting in such a relief valve. G. A. C.

1389. Thermal insulation for industrial requirements. Pt 1. R. Thomas. *Refiner*, 1952, **31** (1), 87–90.—Factors controlling the selection of insulating materials for chemical plant are discussed. A. R. H.

1390. Forces for out-of-plane displacements in L-type bends. F. E. Wolosewick. *Refiner*, 1952, **31** (1), 121.—A method is described for estimating the flexibility of L-type bends in a plane perpendicular to the bend. A. R. H.

Distillation

1391. How to train refinery engineers in distillation. J. C. Chu. *J. Inst. Petrol.*, 1951, **37**, 605–32.—A literature guide and a précis of the subject matter to form an advanced course in distillation, suitable for academic institutions and refineries training technologists in distillation. Approximately 400 references are quoted. A. R. W. B.

1392. Technique of vacuum still operation. Q. E. Benedict. *Refiner*, 1952, **31** (1), 103–6.—Vacuum distillation is discussed, with special emphasis on proper operation

and methods of resolving common operating problems. Three typical examples are given of vacuum-still operation with temp, pressures, flow rates, and inspection facilities. A. R. H.

1393. Statistical thermodynamics of the transition region between two phases. II. One component system with a plane interface. T. L. Hill. *J. chem. Phys.*, 1952, **20** (1), 141–4.—An approx statistical theory is used to investigate the nature of the density transition curve in passing from a one-component liquid phase to the equilibrium vapour phase. This density curve is related thermodynamically to the surface tension, the surface energy, the location of the surface of tension, and to the dependence of surface tension on curvature. (Author's abstract.) E. J. C.

1394. Patents. U.S.P. 2,575,051 (9.7.45; 13.11.51). C. J. Egger and R. H. Webster, assrs to Buckeye Laboratories Corp. Fractional distillation of oil under reduced pressure in which the oil is preheated sufficiently to vaporize the highest-boiling constituent to be removed and is then spray atomized from the bottom of the chamber on to an exposing surface near the top, heat being supplied through the side walls to prevent condensation of the volatile constituents. The oil reaching the exposing surface forms a thin film on it which is exposed to heat and reduced pressure of the chamber and is then returned to the bottom of the chamber and withdrawn. V. P. P.

Ger.P. 824,785, 8.11.51. (G. W. Oetjen and R. Jaeckel.) Leybold's Nachf., Köln. Procedure for obtaining the thinnest possible films on evaporator surfaces in high-vacuum distillation.

Ger.P. 824,787, 8.11.51. (W. Münz.) Dr C. Otto and Comp. Procedure and arrangement for separating liquid mixtures by distillation.

Ger.P. 824,788, 8.11.51. (A. Haltmeier.) Farbenfabriken Bayer. Procedure and arrangement for the separation of volatile materials.

Ger.P. 824,790, 8.11.51. Standard Oil Development Co. Bubble tray and bubble-tray column.

Ger.P. 825,294, 15.11.51. (K. Sondermann.) Process and arrangement for the distillation or rectification, especially of higher-boiling liquids, or for the treatment of higher-boiling liquids with steam or other vapours.

Ger.P. 825,119, 15.11.51. F. Uhde K.-G. u. Westf. App.-Bau-u.-Vertr.-G.m.b.H. Evaporation installation for liquid low-boiling fuels.
Brennstoff-Chem., 1951, **32** (23–4).

Ger.P. 826,747, 29.11.51. (G. W. Oetjen and R. Jaeckel.) E. Leybold's Nachf. Procedure and arrangement for separation of substances with different vaporization rates through distillation at low residual gas pressures.

Ger.P. 826,748, 29.11.51. (H. Miessner.) Farbenfabriken Bayer. Column for distillation, rectification, or adsorption.

Ger.P. 826,749, 29.11.51. (W. Fischer and F. Bauerfeld.) Ges. F. Teerverwertung. Adiabatic column.

Ger.P. 827,492, 6.12.51. (F. Schnur and A. Krauel.) Ruhrchemie. Column trays for filler-absorption towers, especially for the absorption of nitrous gases.
Brennstoff-Chem., 1952, **33** (1–2). R. T.

Absorption and Adsorption

1395. Dehydration of natural gas by glycol injection. J. H. Sullivan. *Oil Gas J.*, 3.3.52, **50** (43), 70.—General applications of glycol injection used in conjunction with low-temperature separation are discussed, with uses and flow-process involved in the system.

Performance data are presented on a 50 million cu. ft. gas/day unit operated by Atlantic Refining Co. at Mustang Island, Texas. G. A. C.

1396. How to design a gasoline plant for sub-zero weather. E. L. Sterrett and H. L. Bretz. *Oil Gas J.*, 3.3.52, **50** (43), 72.—Plant described, designed to process 12,500

million cu. ft. gas/day with an overall propane recovery of 60%, is operated by Ohio Oil Co. in Nebraska. The low-pressure system is buried 3 ft to minimize freezing, and the high-pressure system is 5 ft down. Small indirect heaters (250,000 to 500,000 B.Th.U/hr) have been installed 150 ft from each high-pressure well so that gas can be heated sufficiently to arrive at plant above hydrate temperature.

Fire-protection, product storage, steam, and cooling systems are briefly described, and a flow sheet given. G. A. C.

1397. Patents. U.S.P. 2,572,866 (18.12.47; 30.10.51). I. P. Jones, assr to Standard Oil Development Co. High V.I. paraffinic and naphthenic constituents are removed from lub oil diluted with a C_{3-10} paraffin, b.p. 100° to 300° F, by adsorption on silica gel which is regenerated by washing with the boiling paraffin.

U.S.P. 2,573,341 (19.12.46; 30.10.51). L. Kniel, assr to Lummus Co. Separating C_2H_4 from gaseous mixtures by absorbing most of CH_4 and all higher-boiling material in an aromatic hydrocarbon oil while removing H_2 and CH_4 overhead, the bottoms (CH_4—free) being separately rectified to remove $C_{>3}$ hydrocarbons overhead from which CH_4 and some C_2H_4 are separated and recycled to the absorber while the bottoms are separately rectified to recover pure C_2H_4.

U.S.P. 2,574,434 (4.6.49; 6.11.51). A Greentree and D. A. Hermanson, assr to Socony-Vacuum Oil Co. Inc. Pet. hydrocarbon mixture is contacted with porous adsorbent particles of specified pore size which is such that only the less viscous, light-coloured components are absorbed, the absorbent then being separated, heated to 200° F, and solvent extracted.

B.P. 660,017 (11.10.47; 31.10.51). Lever Bros. and Unilever Ltd. Separation of fatty oils or their derivatives by dialysis through a membrane of a high polymer such as rubber, which swells with the substance to be dialysed or with the solvent used.

B.P. 661,374 (1.4.47; 21.11.51). Lever Bros. and Unilever Ltd. Oil-soluble substances are separated by contacting with a finely divided selective elastomer absorbent such as rubber, P.V.C.—*e.g.*, separation of saturated and unsaturated oils or fatty acids, and of benzene and *n*-hexene. V. P. P.

Ger.P. 824,786, 8.11.51. (W. Tyerman and F. Wrigley.) I.C.I. Ltd. Procedure and arrangement for selective absorption and separation of vapours and gases.

Ger.P. 825,393, 15.11.51. (W. Krah.) Metallgesellsch. Procedure for the separation of materials from gases by means of absorbents.

Ger.P. 825,538, 15.11.51. Comp. Metaux d'Overpelt-Lommel S.A. Procedure and arrangement for separating fine solid, liquid, or misty particles suspended in gases or gas mixtures.

Ger.P. 825,991, 22.11.51. (E. Schön.) Dr C. Otto and Comp. Procedure for the indirect recovery of ammonia from hot gases.
Brennstoff-Chem., 1951, **32** (23–4).

Ger.P. 829,738, 27.12.51. (E. Karwat.) Ges. f. Linde's Eismaschinen. Process for the separation of acetylene from low-cooled or liquefied gases by adsorption.
Brennstoff-Chem., 1952, **33** (1–2). R. T.

Solvent Extraction and Dewaxing

1398. Diffusion through an interface–binary system. L. H. Tung and H. G. Drickamer. *J. chem. Phys.*, 1952, **20** (1), 6–10.—Apparatus and experimental procedure are described for studying the mechanism of molecular motion through an interface for the system SO_2–*n*-heptane using S^{35} tagged SO_2 as a radioactive tracer. It was found that the interfacial resistance was significant compared with resistance to ordinary diffusion, even within 4° C of the critical solution temp. E. J. C.

1399. Diffusion through an interface-ternary system. L. H. Tung and H. G. Drickamer. *J. chem. Phys.*, 1952, **20** (1), 10–12.—Diffusion measurements were made at 22° C and at 44° C in the system phenol–H_2SO_4–water using S^{35} tagged H_2SO_4 as a tracer. The results indicated considerable interfacial resistance and suggested that

the solution chemistry of the system was complex. The apparatus is described, and the results discussed with relation to practical mass-transfer problems. E. J. C.

1400. Extraction of polyhydroxy compounds from dilute aqueous solutions by cyclic acetal formation. 1. An investigation of the scope of the process. R. R. Tink and A. C. Neish. *Canad. J. Tech.*, May 1951, **29** (5), 243–9.—*n*-Butylaldehyde plus a little hydrochloric acid effectively extracts most of the diol from dilute aqueous solutions of 2 : 3-butanediol, similarly, also glycerol, sugars, and sugar alcohols. It is particularly effective with mannitol, sorbitol, adonitol, dulcitol, 2 : 3-butanediol. When 99% of these compounds could be removed from a 4% aqueous solution by one treatment, considerable difference in extraction was found amongst the sugars. Butraldehyde proved to be the best solvent of twelve carbonyl compounds tested. N. T.

Cracking

1401. New platformer improves octane rating. A. L. Foster. *Petrol. Engr*, Feb. 1952, **24** (2), C39–42.—The 1500-b.d. platforming unit at Fort Worth and its operation are described. The reforming is carried out in a three-reactor system, where the charge is successively heated to 900° to 920° F and reacted three times. The third reactor is the largest to give the longest time of contact and hence the max reaction of the charge. Yields of 90 to 95% of the naphthas charged are obtained as reformed gasoline. E. K. J.

1402. Patents. U.S.P. 2,573,245 (31.5.49; 30.10.51). C. A. Boyd and J. Hirschfelder, assrs to Wisconsin Alumni Research Foundation. Efficiency of a solid catalyst is evaluated by exposing it to radiation and then comparing the luminescence on heating with a standard.

U.S.P. 2,573,481 (26.6.47; 30.10.51). L. E. Olson, assr to Sinclair Refining Co. Production of gasoline by cracking hydrocarbon oils in presence of a cracking catalyst containing BaO_2.

U.S.P. 2,573,149 (20.11.48; 30.10.51). L. S. Kassel, assr to Universal Oil Products Co. Reforming process in which gasoline hydrocarbons are passed through three successive bodies of catalyst, in (1) at 750° to 1000° F adiabatically to remove C-forming constituents, in (2) to effect endothermic aromatization using radiant heat, in (3) hydro-cracking adiabatically.

U.S.P. 2,573,906 (18.12.44; 6.11.51). L. C. Huff, assr to Universal Oil Products Co. Production of hydrocarbons by distilling a fluidized mixture of a bituminous material to which silica and alumina of higher catalytic activity than that naturally present has been added, and separately removing a stream of catalyst particles and a stream of residual bituminous solids.

U.S.P. 2,573,747 (15.12.47; 6.11.51). L. J. Weber, assr to Phillips Petroleum Co. Pebble-heater apparatus.

B.P. 661,105 (17.6.48; 14.11.51). Griffin Processes Ltd. and W. von Ediger. Gases, including C_2H_2, and C black are produced by electropyrolysis of liquid hydrocarbons by intermittent electric-arc discharges therein between a multiplicity of C granules immersed between electrodes in the liquid. V. P. P.

Hydrogenation

1403. Patent. U.S.P. 2,574,331 (29.10.47; 6.11.51). W. T. Knox, assr to Standard Oil Development Co. Unstable pet wax is hydrogenated over a Pt–alumina catalyst at 400°F/15 to 300 p.s.i., using a hydrogenation feed rate of 100 to 200 ft^3 per barrel and a wax feed rate of 0·5 to 2 v/v/hr. V. P. P.

Polymerization

1404. Patents. U.S.P. 2,574,894 (17.11.47; 13.11.51). H. R. Snyder and J. M. Stewart, assrs to Phillips Petroleum Co. Aliphatic conjugated dienes are polymerized in aqueous emulsion in presence of a minor proportion of a mercaptan containing an alkyl thioether group in the β-position.

U.S.P. 2,574,020 (17.6.46; 6.11.51). W. W. Crouch, assr to Phillips Petroleum Co. Emulsion copolymerization of butadiene with another monomer in presence of an oxidn-type catalyst is arrested at the desired stage by adding an alkyl polysulphide containing 3 to 5 S per mol and 2 to 16 C per alkyl group. V. P. P.

Alkylation

1405. Four ideas that improved Cities Service's alkylation unit operation. F. L. Resen. *Oil Gas J.*, 25.2.52, **50** (42), 178.—A series of modifications at the Lake Charles refinery which have curtailed shutdowns, improved quality control, and reduced operating costs is described. Continuous addition of fresh caustic soda to the recycle, feeding of sulphuric acid in series, feeding refrigerant condensate to depropanizer, and a piping tie-in between two alkylation units to reduce loss of propylene to refinery fuel gas during turn-arounds are discussed and flow sheets given. G. A. C.

1406. New continuous acid analyser for sulphuric acid alkylation plants. C. L. Persyn. *Refiner*, 1952, **31** (1), 91–3.—A new continuous acid analyser developed for recording acid strengths in alkylation units is described. Acid bled from the reactor is degassed, separated from alkylate, and flows through a hydrometer jar after temp adjustment. The apparatus has a process lag of about 10 min, and permits closer control than conventional sampling methods. A. R. H.

1407. Patent. Ger.P. 825,397, 15.11.51. (C. Wulff and H. Steinbrink.) Chemische Werke Hüls. Method for the production of alkylated aromatic hydrocarbons chlorinated in the nucleus.
Brennstoff-Chem., 1951, **32** (23–4). R. T.

Isomerization

1408. Patent. Ger.P. 825,396, 15.11.51. (J. Anderson, S. H. McAllister, and E. Ross.) N.V. de Bataafsche Petroleum Mij. Process for the isomerization of hydrocarbons.
Brennstoff-Chem., 1951, **32** (23–24.) R. T.

Chemical and Physical Refining

1409. Better sulphur removal. G. Weber. *Oil Gas J.*, 17.3.52, **50** (45), 169.—The new catalytic desulphurization " Autofining " process developed by Anglo-Iranian Oil Co. in a 350-b.d. pilot plant will be used commercially in the company's Llandarcy refinery in Great Britain.

Process employs a fixed-catalyst bed, operates at pressures of 50 to 200 p.s.i.g., and uses a stable sulphur-resistant catalyst, which is periodically regenerated.

Tables show yields on Middle East gasoline, kerosine gas, and crude oils. G. A. C.

1410. Patents. U.S.P. 2,574,122 (11.3.49; 6.11.51). J. W. Ryder, assr to Standard Oil Development Co. Sweetening of 80° to 420° F pet fractions with aq caustic solution containing alkyl phenolate boiling >420° F obtained by acidifying the caustic extract of a thermally cracked stock boiling 420° to 700° F, and an aromatic mercaptide obtained by acidifying the caustic extract of a cat-cracked fraction.

B.P. 659,393 (12.11.47; 24.10.51). Akt. Separator Nobel. Bleaching earth *A* is separated from oil in a centrifugal separator bowl and the separated earth is passed through a layer in the bowl which consists of a supplemental liquid *B* non-miscible with, and of higher sp. gr. than, the oil, the mixture of *A* and *B* being finally discharged through outlets in the bowl wall. If *B* is water, a wetting agent should be added. V. P. P.

1411. Patents. Fr.P. 985,359, 18.7.51. Humphreys and Glasgow Ltd. and W. C. Holmes and Co. Ltd. Process for purification of gases containing hydrogen sulphide.

Ger.P. 825,868, 22.11.51. (W. Oettinger and H. Nonnenmacher.) Bad. Anilin- & Soda-Fabr. Process for the improvement of highly unsaturated kerosine containing sulphur. (Addition to 802,398.)

Ger.P. 825,871, 22.11.51. (W. Sexauer and O. Bär.) Ruhrchemie A.-G. Gastechnik G.m.b.H. Process for desulphurization of gases in turreted vessels by means of moulded gas-purification masses.

Brennstoff-Chem., 1951, **32** (23–4).

Ger.P. 827,796, 6.12.51. (H. Börner.) Steine u. Erden G.m.b.H., Goslar. Arrangement for the wet dust removal from gases and vapours, especially vapours from lime slaking.

Brennstoff-Chem., 1952, **33** (1–2). R. T.

Special Processes

1412. Economics of sulphur production from hydrogen sulphide. A. L. Kohl and E. D. Fox. *Oil Gas J.*, 25.2.52, **50** (42), 154.—Investment and operating costs of typical sulphur plant are analysed and tabulated, based on data from the Fluor Corporation, U.S.A.

The net cost of production of sulphur as a by-product varies from $8·42/ton for a 20-ton/day plant, to less than $2/ton for a 320-ton/day installation.

A table shows capacity and status of plants in the U.S.A. converting hydrogen sulphide to sulphur. G. A. C.

1413. Petroleum chromatography in analysis and manufacture. H. Weil. *Brennstoff-Chem.*, 1951, **32** (23–4), 357–65.—This, the first of three parts, reviews extensively the principles and history of petroleum chromatography and the relevant activities of international investigators. The work of Engler and Boehm in 1886 on the chem nature of vaseline may be considered as the origin of column chromatography as applied in America to the systematic analysis and fractionation of a mineral-oil mixture. The inceptions and authors of various chromatographic separations are debated. Numerous physical and chem chromatographic laboratory methods, with certain modifications, can be used in bulk separations. Distribution and ion-exchange chromatography have developed into important branches in works technology. Great influence is exerted on petroleum chromatography by the work of the National Bureau of Standards jointly with the API within the framework of Project 6. The chromatographic method was employed, after full development, for the separation of a crude Mid-Continent petroleum into fractions whereby increasingly heavy oils were studied. It was employed further for the splitting up of the fractions into sub-groups or individual constituents. The effect of independent research in other branches on petroleum chromatography is emphasized, and will be dealt with in Pt 2, and Pt 3 will deal with pet technology. Ninety-two literature references. R. T.

1414. Large carbon black plant now operating in Britain. V. S. Swaminathan. *Refiner*, 1952, **31** (1), 124–5. A brief description is given of the carbon-black plant at Avonmouth, producing 50 million lb yearly. A. R. H.

1415. Coal carbonization may open door to commercial synthetic fuels. Anon. *Petrol. Process.*, 1952, **7** (1), 45.—The unique features are discussed of a method for the low-temp carbonization of coal, involving the fluidization technique, developed by the Pittsburgh Consolidation Coal Co. In the process powdered coal is partially converted to a fine char containing about 70% of the original coal cal. val. A tar liquid is distilled off in the conversion stage and refined to yield low-boiling tar acids, creosotes, or feed stock for carbon-black manufacture and electrode carbon, or converted to fuel. D. W. F.

1416. Production of ethylene from petroleum sources. Pt III. P. W. Sherwood. *Refiner*, 1952, **31** (1), 126–30.—(See Abs. No. 198, 501.) The four commercially successful methods for the separation and purification of ethylene from cracked gases are low-temp fractionation, absorption in oil, Hypersorption, and absorption in cuprous salt solutions. The general principles, design considerations, and characteristics of these methods are reviewed. A. R. H.

1417. Patents. U.S.P. 2,574,469 (21.3.50; 13.11.51). R. G. Dressler and J. R. Bircher, assrs to the U.S.A. (Secretary of the Interior). Low-boiling alcohols, aldehydes, and ketones are separated from the aq fraction obtained in the Fischer–Tropsch reaction, and the residual aq solution of organic acids is recycled to the synthesis gas producing zone.

U.S.P. 2,573,185 (20.12.48; 30.10.51). J. S. Cromeans, assr to Phillips Petroleum Co. Resolving the aq phase product of a Fischer–Tropsch process by distilling overhead a mixture of CH_3CHO, Me_2CO, MeOH, and EtOH, extracting the residue with a selective solvent for PrOH, BuOH, AmOH, acetic, propionic, and butyric acids, heating the solvent-free extract with aq mineral acid at 20° to 50° C—to produce Pr acetate and Bu and Am propionates and butyrates from which acetic acid and Pr acetate are distilled off overhead, and adding additional butyric acid to the residue to liberate propionic acid and form Bu and Am butyrates which are separated by distillation.

U.S.P. 2,573,751 (28.8.47; 6.11.51). E. R. Woodward, assr to Mathieson Chemical Corp. Oxidation of $C_{<8}$ hydrocarbons by blowing with ClO_2 + air at <100° C.

U.S.P. 2,574,070 (1.7.48; 6.11.51). R. J. Strawinski, assr to Texaco Development Corp. Complex S compounds in pet are converted to readily removable products by treatment with bacteria of species of *Pseudomonas*, *Alcaligenes*, and *Bacillus*, and then subjecting the products of metabolism to the action of sulphate reducing bacteria of the *Vibrio* species.

B.P. 660,671 (7.1.49; 7.11.51). Humphreys & Glasgow Ltd. and N. H. Williams. Froth is separated into its components by passing it under super-atm pressure through a non-driven centrifugal froth separator, liquid and gas being discharged separately. Separation is caused solely by the pressure of the gas in the froth. The froth is forced tangentially into the separator, which may or may not be rotated by the pressure of the gas.

The following U.S. patents, published 13.11.51, in the names of M. de Groote, alone or with B. Keiser, A. F. Wirtel, O. H. Pettingill, and assigned to Petrolite Corp., are concerned with emulsion breaking or with synthetic resins useful for this purpose :—

2,574,536. Demulsifying with a nuclear hydrogenated oxyalkylated 2 : 4 : 6-C_{4-12} hydrocarbon substituted monocyclic phenol-C_{1-8} aldehyde resin.

2,574,537. Reaction product of diglycol chloroformate and an oxyalkylated imidazoline containing a C_{11-22} substituent.

2,574,538. Demulsifying with a mixture of (*a*) a partial ester of a polyhydric alcohol and a diglycollic acid containing acyloxy radicals derived from C_{8-22} soap forming monocarboxylic acids, at least one being a hydroxy acid and (*b*) an oxyalkylated 2 : 4 : 6-C_{4-18} hydrocarbon substituted phenol–aldehyde resin.

2,574,539–40. Ethers derived from para-menthyl*cyclo*hexanol and ethylene or propylene oxide.

2,574,541–2. Ethers derived from para-*cyclo*hexyl*cyclo*hexanol and ethylene or propylene oxide.

2,574,543. Demulsifying with a reaction product of ethylene or propylene oxide and a phenolic resin derived in part by reaction with an acetylene.

2,574,544–5. Demulsifying with reaction product of an $\alpha\beta$-alkylene oxide with (*a*) allyl sucrose alone or with other allyl compounds (*b*) polymerized penta allyl sucrose.

2,574,546–7. Resin derived by reacting a C_{4-18} hydrocarbon substituted phenol with an aldehyde is oxyalkylated with a $C_{>4}$ $\alpha\beta$-alkylene oxide, the product hydrogenated and then condensed with allyl glycidyl ether, which in 2,574,547, is polymerized and reacted with a $C_{>4}$ $\alpha\beta$-alkylene oxide. In 2,574,817 at least 2 moles of glycidyl ether are reacted for each alicylic mole but not more than three times the numbers of hydroxyl groups present therein. V. P. P.

Ger.P. 824,793, 8.11.51. (L. Raichle and A. Wegerich.) Bad. Anilin- & Soda-Fabr. Process for obtaining *iso*butylalcohol.

Ger.P. 825,398, 15.11.51. (H. Sönksen and K. Bossert.) Bad. Anilin- & Soda-Fabr. Method for the production of compounds containing oxygen, especially alcohols, through reaction of carbon monoxide with hydrogen.

Ger.P. 825,835, 22.11.51. (W. Münster.) Bad. Anilin- & Soda-Fabr. Method for the production of ethylene oxide.

Ger.P. 825,401, 15.11.51. No patentee given. Process for the oxidation of paraffinic hydrocarbons with nitrous gases in the presence of sulphuric acid containing nitrosyl sulphuric acid.

Ger.P. 825,261, 15.11.51. (K. Fehr.) Kohlentechn. G.m.b.H. Process for recovery of pyridine and its homologues from gases, vapours or aq-solutions containing them.

Brennstoff-Chem., 1951, **32** (23–4).

Fr.P. 974,643, 7.9.48. Great Lake Carbon Corp. Improvements to processes for purification of coke or carbon and products obtained.

Brennstoff-Chem., 1952, **33** (1–2). R. T.

Metering and Control

1418. Refinery instruments—what makes them tick? Pt 7—Control valves. C. E. Shannahan. *Petrol. Process.*, 1952, **7** (1), 49–53.—A general description of air-operated diaphragm control valves is accompanied by an exploded view of such a valve. Relative values of air-to-open and air-to-close valves are discussed. Points to be considered in selecting and sizing valves are mentioned, together with the usual valve-capacity formula. Linear and percentage control-valve flow characteristics are illustrated with flow curves for linear, percentage V-port, and percentage parabolic plugs, with diagrams of the last two. A heat-exchanger problem with a by-pass control valve is chosen to illustrate the method of determining the capacity required by the by-pass valve. A three-way valve is described with diagram. D. W. F.

Products

Chemistry and Physics

1419. Correlating physical and thermodynamic properties. Pt II. D. F. Othmer and R. Gilmont. *Refiner*, 1952, **31** (1), 107–16.—(See Abs. 514—1952.) Correlations are described for chemical reaction equilibrium constants, densities of liquids, visc of liquids, visc of gases, surface tension of liquids, and entropies of gases. The methods involve a comparison of the properties of one substance with those of another under the same conditions. A. R. H.

1420. Studies in Newtonian flow. I. Dependence of the viscosity of liquids on temperature. A. K. Doolittle. *J. appl. Phys.*, Aug. 1951, **22**, 1031–5.—A method is presented of developing a visc–temp relationship of *n*-paraffins that gives equations defining this dependence with volatility, which shows that the precise dependence of visc of liquid on temp is complex. N. T.

1421. Flow of gases in porous media. L. H. Witson, W. L. Sibbilt, and M. Jakob. *J. appl. Phys.*, Aug. 1951, **22**, 1027–30.—The equations which describe the phenomena of viscous and free molecular flow are applied to the flow through porous media and are combined to yield a semi-empirical equation which may be used for viscous and free molecular flow and for the transition region between them. Experimental ratios of molecular mean free path to pore dia are given, and they may be used to indicate the nature of flow in porous media when the pore size is known, or they may be used to determine the pore size experimentally. N. T.

1422. Ageing of bentonitic cracking catalysts. J. Holmes and G. A. Mills. *J. Phys. & Colloid Chem.*, Nov. 1951, **55**, 1302–20.—Changes have been measured in the cracking activity as well as the pore structure in Filtrol, an acid-treated bentonitic clay, resulting from air or steam treatment from 510° to 1135° C.

Treating for a 10-hr period in air produces inactivity at 850° C, which is characterized by a loss in surface area and a marked increase in bulk density. A pronounced activity loss was noticed by treating with steam for several hr at 550° C. Complete

loss of activity under these conditions occurred at 790° C. In the case of steam treatment the surface area diminishes at temps at which the bulk density is sensibly constant.

No overall correlation was discovered between cracking activity and surface area, for all the heat-treated samples, although such a correlation existed for each individual series of steam- or air-treated samples.

The cracking activity does not seem to be related to any phase which appears crystalline to X-rays. Precalcination at 565 made filtrol samples much more susceptible to loss in activity upon steam treating than in the case where there was no pretreatment.

N. T.

1423. Residual hydrogen on synthetic ammonia catalyst. J. T. Kummer and P. H. Emmett. *J. Phys. & Colloid Chem.*, Mar. 1951, **55**, 337–45.—Promoted iron catalysts, but not pure iron catalysts, retain sufficient hydrogen after 24 hr evacuation at high temp (~ 500° C) to be equivalent to the covering of 5 to 35% of the metallic surface, or 1 to 10% of the part of the surface covered with promoters. Due account should be taken of this residual in any absorption measurements on promoted iron catalysts.

N. T.

1424. Two types of inhibition of the hydrogen–oxygen reaction by hydrocarbons. R. R. Baldwin, N. S. Corney, and R. M. Precious. *Nature*, 1952, **169**, 201.—With propane, as with higher hydrocarbons, the second explosion limit of H_2–O_2 mixtures is depressed proportionately to the propane concentration; with methane the limit is almost unaffected up to a molar concentration of 2·5%, and thereafter the explosion is completely suppressed.

For propane the concentration required to reduce the limit by 50% is proportional to the O_2 concentration and independent of the H_2 concentration, dia of the reaction vessel, and the nature of the surface. The critical concentration for methane is approx proportional to the O_2 concentration and almost independent of the H_2 concentration and of the nature of the surface. It increases as the dia of the vessel is increased. In the case of methane inhibition is thought to proceed through the intermediate formation of HCHO, for analyses of mixtures which have not exploded show that significant amounts of methane have been oxidized.

H. C. E.

1425. Synthesis of hydrocarbons and oxygen-containing compounds from water and carbon monoxide. H. Kölbel and F. Engelhardt. *Erdöl u. Kohle*, 1952, **5**, 1–9.—Work described concerns the single-stage formation with good yields of stable liquid hydrocarbons and oxygenated compounds from CO and H_2O. Previous workers had shown that it was possible to obtain gaseous hydrocarbons directly from mixtures of CO_2 and H_2. Similarly, good yields of stable liquid hydrocarbons were obtained from CO_2 and H_2 in single-stage synthesis on Fe cat. From thermodynamic considerations of various reactions between CO, CO_2, and H_2 or H_2O, their heats of reactions, free energies, and equilibrium const it is shown that in the case of hydrocarbon synthesis from CO and H_2O: (1) Heat of reaction per mol CH_2 radical produced increases by a const amount (approx + 9·5 k.cal/mol), ascending in the following order: (*a*) reduction of CO_2 with H_2 (29·9 k.cal/mol); (*b*) Fischer–Tropsch synthesis of CO and H_2 yielding H_2O (39·4 k.cal/mol); (c) as (*b*), but yielding CO_2 instead of H_2O (48·9 k.cal/mol); (*d*) the new synthesis of CO and H_2O (58·4 k.cal/mol). The const increase in heat of reaction is equivalent to that of the water–gas reaction; it is evident that the heat of reaction increases with consumption of CO and decreases with that of H_2. Heat of reaction (for hexane) at synthesis temp of 227° C is 59·8 k.cal per mol CH_2 radical, which exceeds by almost 20 k.cal/mol that of the classical Fischer–Tropsch reaction with H_2O as oxidation product. (2) Affinity of CO–H_2O reaction, measured in terms of increase in free energy of system, is greater than the corresponding Fischer–Tropsch reaction. Free energy also varies by const factor as does heat of reaction. (3) According to equilibrium const synthesis of hydrocarbons from steam and CO is possible at temp up to 500° C, or 100° C higher than by Fischer–Tropsch. The various reactions discussed always vary in the temp at which their equilibrium const equals unity by a multiple of 50° C. The range of results and operating conditions covered by the authors was as follows: temp 150° to 400° C, optimum 210° to 260° C; pressure 0 to 100 atm; space velocity (*i.e.*, gas throughput) up to 1000 and more; water vapour to CO ratio $<0·5$; cat investigated Fe, Co, Ni, and others; H_2O conversion $>90\%$; CO conversion $>90\%$; H_2O/CO consumption ratio 1 : 3 to 1 : 2; yields to date up to 216 g hydrocarbon + oxygenated compounds

per m³ of CO used; composition of products: paraffin hydrocarbons (methane to hard paraffin), up to max 60% olefins, and up to max 40% oxygen-containing compounds in total products. Experimental work over period of several years is described, influence of many variables on properties and yields of products studied. Wide possible application of this type of important new synthesis is stressed. P. V.

1426. Extraction of polyhydroxy compounds from dilute aqueous solutions by cyclic acetal formation. II. Batch extraction of glycerol. R. R. Tink, E. Y. Spencer, and J. M. Roxburgh. *Canad. J. Tech.*, May 1951, **29**, 250–60.—Using butraldehyde the amount and rate of extraction of glycerol from dilute aqueous solutions has been studied. The amount of free and combined glycerol in the aqueous phase at equilibrium is proportional to the initial glycerol concentration, and increases with increasing temp. The reciprocal of the residual glycerol concentration is a linear function of the ratio of butraldehyde to water. The rate of extraction increases linearly with the mineral-acid concentration. The same linear increase in rate is observed with increasing amounts of cation exchange resins as catalysts.

The rate of extraction increases with temp and with increasing *n*-butraldehyde-to-water ratio. N. T.

1427. Second limit of hydrogen–oxygen mixtures by the withdrawal method. R. R. Baldwin and R. M. Precious. *Nature*, 1952, **169**, 290.—Pre-mixed hydrogen–oxygen mixtures do not explode at temp between 460° and 500° C in clean Pyrex vessels if the pumping speed is below a critical value. When oxygen is partially replaced by nitrogen the critical speed for no explosion is reduced. This effect is absent in KCl-coated vessels. If the explosion limit is approached by increasing the temp, the pressure gradually increases due to thermal expansion, becomes steady at the expected explosion temp, then falls slightly as the temp is further increased.

This effect can be explained if water is regarded as inhibiting the explosion, and this possibility is developed mathematically. One of the self-inhibiting mechanisms discussed may also account for the inhibiting action of methane. H. C. E.

1428. Production of sulphur trioxide during the combustion of carbon in air containing small quantities of sulphur dioxide. G. Whittingham. *Nature*, 1952, **169**, 155.—Carbon tubes of 1 cm I.D. inside a quartz tube were burned in a stream of dry air containing 0·08% vol SO_2. The SO_3 content of the exit gases was estimated by the dew-point technique.

When the temp of the quartz tube was increased by 10° C/min the SO_3 content increased rapidly between 730° and 780° C, and a blue glow, having the flame spectrum of CO, was seen. At 900° C with a 1-cm carbon tube the dew point first showed a slight increase, then remained constant until *ca* 80% of the C was consumed; thereafter it rapidly decreased. With longer tubes the initial dew point was lower than with a 1-cm tube, but it gradually increased as the C was consumed, and eventually the behaviour was the same as with a 1-cm tube.

These results are explained as follows: At temps above *ca* 600° C CO is the major primary product, and this burns to CO_2. Under given conditions the gas therefore contains no free O_2, and in long tubes the SO_3 produced in the first part of the tube during combustion of the CO then undergoes reduction at the carbon surface. This reduction is probably very rapid at temps between 800° and 900° C. H. C. E.

1429. Monisotropic propagation of combustion waves in explosive gas mixtures and the development of cellular flames. J. Manton, G. von Elbe, and B. Lewis. *J. chem. Phys.*, 1952, **20** (1), 153–7.—Phenomenon of non-isotropic propagation consists in the spontaneous development of blisters or cells on the surface of a combustion wave. The experiments described on spherical flames and those carried out by Markstein (*J. chem. Phys.*, 1949, **17**, 428) show that the phenomenon is characteristic of non-stoichiometric explosive mixtures in which the deficient reactant constituent is also the constituent of largest diffusivity. This suggests that the blisters are caused by the effect of diffusion processes on burning velocity. In curved areas of the wave that are convex with respect to burned gas, burning velocity is reduced because lines of diffusion diverge and concentration of the faster-diffusing constituent decreases, whereas in concave areas the lines of diffusion converge and the concentration of the

faster diffusion constituent increases. In rich mixtures of hydrocarbon and oxygen additional evidence for the effect is furnished by the emergence of carbon streamers and by characteristic changes of light emission from convex wave areas, showing that the oxygen concentration, and probably therefore the burning velocity, is decreased in these areas below the average for the mixture. E. J. C.

1430. The flow pattern of gas turbine combustion. F. H. Garner and H. A. Cheetham. *J. Inst. Petrol.*, 1951, **37**, 554–66.—The design of a small-scale laboratory gas-turbine combustion chamber to burn about 50 ml of fuel/hr is described. With this apparatus the flame temp and flame stabilities of propane, petroleum ether, *iso*-octane, heptane, and benzene have been measured over a range of pressures from 100 mm Hg to atmospheric and the results are discussed. A. R. W. B.

1431. An experimental study of the evaporation and combustion of falling droplets. J. E. C. Topps. *J. Inst. Petrol.*, 1951, **37**, 535–53.—A general investigation of the evaporation of droplets of 300 to 500 μ dia falling at their terminal velocity in high-temp atmospheres showed a rate of evaporation for pure hydrocarbons dm/dt which varied approx as radius $^{1\cdot6}$. It is concluded that in gas-turbine practice less advantage will be obtained by securing fine atomization than is to be expected from simple theory which suggests that dm/dt varies as radius $^{2\cdot5\,(2\cdot3)}$. This discrepancy is discussed. A. R. W. B.

1432. A unified picture of diffusion. J. D. Babbitt. *Canad. J. Phys.*, 1951, **29**, 427.—The author shows that if the equation

$$\frac{\partial p}{\partial x} - A_x = 0$$

(where p is a pressure function and A_x a resistive force) is taken as the fundamental dynamical equation, then it is possible to explain diffusion in solutions, in solid solution, and in an adsorbing solid as well as the inter-diffusion of two gases. In diffusion in both liquid and solid solutions the pressure function is the osmotic pressure; in diffusion of adsorbed gases the pressure function is the spreading pressure of the adsorbed layer. To evaluate A_x, however, it is necessary to assume a specific physical mechanism for the movement of the mols. S. B.

1433. On the diffusion of adsorbed gases through solids. J. D. Babbitt. *Canad. J. Phys.*, 1951, **29**, 437.—The equations for the diffusion of an adsorbed gas through a solid are developed on the assumption that the resistive force is directly proportional to the number of molecules adsorbed, *i.e.*, that the resistive force per molecule is constant. In a previous paper (Abs. 629—1951) the author developed equations assuming that the resistive force per mol is inversely proportional to the number of mols adsorbed. In the present paper the author compares both sets of equations with each other and with experiment, and concludes that the equations developed here are not as satisfactory as those developed earlier. It is pointed out that this is a consequence of the fact that heats of adsorption have been found experimentally to decrease as the amount of adsorbed gas increases. S. B.

1434. Interfacial tension of some hydrocarbons against water. W. E. Rose and W. F. Seyer. *J. Phys. & Colloid Chem.*, Mar. 1951, **55**, 439–47.—The interfacial tensions of several cyclics and normal paraffins against water have been measured between 20° and 70° C by the differential bubble-pressure method; it appears to be a linear function of temp over this range.

Antonaff's rule is closely obeyed by octane and decane, for which the difference between work of cohesion and that of adhesion approaches zero. N. T.

1435. Sorption hysterisis, I. A. G. Foster. *J. Phys. & Colloid Chem.*, May 1951, **55**, 638.—A review of existing data on sorption hysterisis shows that the size of the loop decreases with increasing temp and with increasing dia. Both these predictions are in complete agreement with the open-pore theory. N. T.

1436. Sorption of gases on metals at room temperatures. A. L. McClellan and N. Hackerman. *J. Phys. & Colloid Chem.*, Mar. 1951, **55**, 375–82.—Isotherms for the sorption of oxygen, chlorine, nitrogen monoxide, and nitrogen dioxide at 30° C, on reduced and unreduced surfaces of steel, 18 chromium and nickel stainless steel, and pure chromium powders have been determined. Reduction by hydrogen treatment increased the uptake of both oxygen and chlorine on steel, but not with the passive metals, on which no more than six equivalent layers of gas were sorbed. Calculation showed that a 50 Å ferrous oxide layer formed on unreduced steel exposed to oxygen, and at 110 Å layers formed on reduced steel. N. T.

1437. Radioactive isotopes in petroleum research. Anon. *Petroleum*, Mar. 1952, **15** (3), 61–6.—The major uses in petroleum research of both naturally occurring and artificially produced radioactive isotopes are surveyed. These include :—

Oil-well studies, e.g., (1) Oil-well-logging studies using γ activity of formation and that induced by neutron irradiation of the surrounding formation by a *Ra Be* source. (2) γ-ray logging is also used to determine the exact height to which cement has risen behind the well casing. (3) Tracer application in the study of fluid distribution, in sand, oil, and water mixtures, and to study the permeability of naturally occurring or artificially produced porous media to the flow of oil, gas, and water mixtures.

Crude-oil recovery. Isotopes are useful in water displacement of oil to detect places of break-through into operating well, and also in controlled acid treatment of oil-bearing rocks to overcome clogging with limestone, thus avoiding considerable waste of acid.

Pipeline applications include location of stuck pipeline scrapers used to remove wax from inside pipes and to determine the position of the interface between two products. It is suggested that fundamental studies of flowing liquids, measurement of velocities and volumes could be carried out using isotopes.

Refinery equipment includes the Levelometer, a reflection-type gauge for the determination of liquid level inside tanks ; the Penetron, used to determine liquid level or specific gravity and for the detection of internal corrosion in pipelines, storage tanks, etc. ; and the Gagetron, used to indicate and control catalyst level in cracking-unit vessels.

Refining and synthesis investigations. Labelled hydrocarbons, *e.g.*, C^{14}, are used to determine mechanism of hydrocarbon conversion of Fischer–Tropsch synthesis, etc., and also to investigate the path followed and poisoning of catalysts in catalytic processes.

Isotopes have also been used to determine separation efficiency in distillation ; to study the effect of water on asphalt coatings ; detergent studies ; for a number of lubricating-oil applications ; and to investigate the mechanism of fuel oxidation. R. E. P.

1438. Some results on the electrical breakdown of liquids using pulse techniques. W. D. Edwards. *Canad. J. Phys.*, 1951, **29**, 310.—The apparatus is so constructed that the liquid may be distilled and the breakdown measurements made within a completely enclosed system and at pressures less than atmospheric when desired.

Single rectangular pulses of voltage are applied to a pair of highly polished metal spheres immersed in the test liquids, and time delay in breakdown of the order of 1 μ sec, the exact value depending on the width of the gap, have been found for the liquids used, which included simple polar and non-polar organic compounds. In the liquid state hexane and ethyl alcohol were found to have negative temperature coefficients of breakdown strength, while the breakdown strength of benzene was found to depend on the cathode metal but was independent of the anode metal. A reduction in gap width gave rise to an increase in breakdown strength for benzene and *n*-hexane. The results do not give any information on the time required for the few electrons originally present to gain energies sufficient to ionize the liquid mols, except to indicate that it is less than 0·1 sec, the length of the shortest pulse used. S. B.

1439. Patents. Ger.P. 825,839, 22.11.51. (W. Stein and H. Hartmann.) Henkel & Cie. Process for the separation of mixtures of synthetic higher-molecular fatty acids into constituents with different melting points.

Ger.P. 825,403, 15.11.51. (B. Jüttner.) Kohlentechn. G.m.b.H. Procedure for the production of aromatic carboxylic acids through preliminary treatment of fuels as well as of their treatment products and subsequent oxidation.

Ger.P. 825,552, 15.11.51. (H. Ratte, E. Schweym, and J. Geller.) Rütgerswerke A.-G. Procedure for recovery of technically pure constituents from liquids.
Brennstoff-Chem., 1951, **32** (23–4).

Ger.P. 826,592, 29.11.51. (W. Reerink) Kohlentechn. G.m.b.H. Process for the utilization of petroleum small coke.

Ger.P. 828,397, 13.12.51. (W. Demann.) Kohlenwertstoff-A.-G. Process for producing pitch coke poor in zinc.
Brennstoff-Chem., 1952, **33** (1–2). R. T.

Analysis and Testing

1440. Direct determination of oxygen in organic compounds. Carbon reduction—manometric method. J. Holowchak and G. E. C. Wear. *Anal. Chem.*, 1951, **23**, 1404–7.—An apparatus and procedure have been developed for the direct determination of oxygen in organic compounds by a manometric modification of the Unterzaucher carbon-reduction method, in order to circumvent difficulties due to reaction of hydrogen formed by pyrolosis and reduction of organic material with iodine pentonide. Interference of hydrogen was especially troublesome in the analysis of hydrocarbons containing small amounts of oxygen. The modified procedure involves oxidation of the carbon monoxide to carbon dioxide by means of copper oxide collection of the carbon dioxide in a liquid nitrogen trap, and, after the residual gases have been pumped out by means of a vacuum pump, determination of the carbon dioxide manometrically in a standard volume. Hydrogen is concurrently removed as water and frozen out in a dry ice trap. The method is self-contained, has greater sensitivity, and is not subject to erroneously high results on samples of low oxygen content due to hydrogen interference. J. S.

1441. Determination of oxygen in organic materials by modified Schutze-Unterzaucher Method. Application to petroleum products. M. Dundy and E. Stehr. *Anal. Chem.*, **23**, 1408–13.—The Schutze-Unterzaucher method was investigated because high results were obtained when certain lots of iodine pentoxide were used in the determination of oxygen; analysis of hydrocarbon samples indicated oxygen contents as high as 2·5%. Data indicate that this anomoly is caused by liberation of extraneous iodine from the iodine pentoxide through the partial reaction of the oxidant and the hydrogen formed by pyrolysis of the sample. A gravimetric procedure precludes interference due to extraneous iodine. The iodine is retained in an absorption tube containing crystals of sodium thiosulphate and suitable drying agents. The carbon dioxide is weighed by conventional means in a Pregl micro-absorption tube. Improvements in apparatus and experiences of both methods are described. J. S.

1442. Improved method for the determination of oxygen. V. A. Campanile, J. H. Badley, E. D. Peters, E. J. Agazzi, and F. R. Brooks. *Anal. Chem.*, 1951, **23**, 1421–6.—The Schultze-Unterzaucher method for the determination of oxygen, by reduction over carbon at 1120° C, has been studied for the purpose of developing a reliable method for routine use. A convenient unitized apparatus has been designed, and a procedure which is applicable to a wide variety of materials has been developed. Hydrogen was found to interfere seriously with the determination of small amounts of oxygen in hydrocarbon mixtures, by virtue of its slow reaction with iodine pentoxide; this interference was surmounted by removal of the hydrogen by diffusion through a heated palladium thimble. The resulting method retains the simple and sensitive iodometric titration in the concluding step. Results are presented for the analysis of a variety of materials to illustrate the wide scope of the method. J. S.

1443. Portable meter for determining dissolved oxygen. For use with oil-field brines. G. A. Marsh. *Anal. Chem.*, 1951, **23**, 1427–31.—The standard Winkler method for determining dissolved oxygen yields unreliable results with many oilfield brines because of the presence of high concentrations of magnesium, calcium, and ferrous

salts. A method was described which would permit rapid and convenient determination of dissolved oxygen in the field, principally to check the operation of brine-treating plants. A sample portable polarographic instrument was developed using a rotating platinum micro-electrode. Dissolved oxygen measurements can now be made in natural brines with an accuracy of $\pm 5\%$. The instrument makes possible a convenient study of the efficiency of aeration and de-aeration in brine-treating plants. Another important use is in estimating corrosiveness of brine without requiring long-term corrosion tests. J. S.

1444. Mass spectrometry as aid in chemical analysis. H. Luther and L. Jenckel. *Erdöl u. Kohle*, 1952, **5**, 17–24.—Development of mass spectrometers, their theory, construction, operation, and functions are described. Wide application of mass spectroscopy in chemical analysis to date is described, and its results are compared with those of infra-red and u.v. analysis techniques. Thirty-three references. P. V.

1445. Some criteria for commercial spectrometers. Pt II. Comments by manufacturers. J. G. Reynolds. *J. Inst. Petrol.*, 1951, **37**, 588–95.—The criticism and advice of four American and three British manufacturers of spectrometers, to whom Pt I of this paper was submitted, is recorded. A. R. W. B.

1446. Determination of iron in used lubricating oils by spectrochemical analysis. J. Hansen, P. Skiba, and C. R. Hodgkins. *Anal. Chem.*, 1951, **23**, 1362–5.—A rapid and accurate method for the quantitative determination of a wide range of iron content in used lubricating oils is useful when extensive engine wear or performance studies are being undertaken. A spectro-chemical procedure capable of yielding accurate analyses of 3 to 3000 p.p.m. of iron in used lubricating oils is described. A fixed quantity of internal standard is added to a weighed amount of sample, and 10 drops of the resulting mixture ashed in the cavity of an electrode. The electrode is designed so that the cavity wall can be easily removed to expose the ash on a conical tip. Satisfactory results have been obtained using as little as 5 g of sample. The overall accuracy of the method is within approximately $\pm 5\%$ of the amount present. J. S.

1447. Infra-red spectrophotometric determination of oils and phenols in water. R. G. Simard, I. Hasegawa, W. Bandaruk, and C. E. Headington. *Anal. Chem.*, 1951, **23**, 1384–8.—The petroleum industry has long been concerned with the elimination of both hydrocarbon oil and phenols from its effluent waters. None of the analytical methods currently in use has both the sensitivity and accuracy desired, and as part of the petroleum industry's pollution-abatement programme, a sensitive, accurate infra-red method has been devised for determining small amounts of oil and phenols in water. The method is based on bromination of the phenols, extraction of resulting bromides from water with carbon tetrachloride, and measurement of optical density of the extract at 2·84 μ where absorption is due to O–H vibration when intramolecular hydrogen bonding of the bromine and hydroxyl groups takes place. The oil determination is based on optical density of the same extract at the CH_3, CH_2, and CH stretching frequencies in the region of 3·4 μ. The method for oil is sensitive to 0·1 p.p.m. Less than 10 parts per billion of phenols can be determined with reasonable accuracy. J. S.

1448. Spectrographic determination of metal contaminants in cracking catalyst. Characteristic of arc excitation. E. L. Gunn. *Anal. Chem.*, 1951, **23**, 1354–8.—The moving-plate technique has been employed to investigate the spectrographic excitation characteristics of contaminants and added internal standard elements in cracking catalysts. Measurement of the degree of similarity in behaviour exhibited by internal control elements during excitation shows that arcing the sample to depletion does not result in improved precision over that obtained by a somewhat shorter period of excitation. The basic composition of the catalyst influences the excitation characteristics exhibited by the contaminant elements. J. S.

1449. Spectroscopic determination of vanadium in residual fuel oils. J. W. Anderson and H. K. Hughes. *Anal. Chem.*, 1951, **23**, 1358–61.—A spectroscopic method has

been developed using a direct-current arc for the determination of vanadium in residual fuel oils and other petroleum products. Vanadium is not lost during the controlled ashing which is part of the procedure. Fuel oils containing from 0·0004 to 0·045% vanadium have been analysed. The use of a titanium internal standard and a matrix of silica and graphite extends the method to most ashes or powders containing more than 1% vanadium. J. S.

1450. Quenched electrode procedure in spectrographic analysis. As applied to new detergent type oils. R. O. Clark. *Anal. Chem.*, 1951, **23**, 1348–53.—A report published in 1946 by Calkins and White, on a quenched-electrode technique for the spectrochemical analysis of lubricating oils for the determination of the amount of additive metal content, directed the attention of a group of oil laboratories to the method as a possible improvement over conventional chemical procedures. Investigation of the method revealed that it is satisfactory for refinery control purposes, *i.e.*, where specific base oils and additives are available for calibration. Experimental results, however, indicate that the method is not applicable to used oils, to oils of unknown base stock, or to unknown additive material. In an effort to extend the scope of the technique, several petroleum laboratories undertook a co-operative investigation of the variables inherent in the quenched-electrode principle. The material presented includes details of, and conclusions deduced from, this investigation. Although the objective of extending the utility of the method was not achieved, the information presented represented a contribution to applied spectroscopy, and should be of value to other investigators undertaking similar programmes. J. S.

1451. Determination of total alkyl benzenes in selected crude fractions. An ultra-violet method. J. F. Kinder. *Anal. Chem.*, 1951, **23**, 1379–82.—Solvent properties of petroleum fractions, interest in petro-chemicals, and expanded output of heavier fuels have demanded additional information as to the aromaticity of crude fractions boiling above 300° F. An application of ultra-violet analytical methods for a rapid estimate of total aromatics in petroleum crude cuts which have a boiling range of 200° to 395° F is described. The basis of the test is the use of an average aromatic absorptivity calculated at a wavelength of 215 mμ. Typical analyses and comparisons with ASTM D 875-46T acid-absorption procedure are given for fractions from three crudes. The ultra-violet procedure is not designed for crude fractions containing benzene and/or naphthalene; both of these compounds are removed readily by distillation. To date, the analytical data have been obtained from petroleum stocks which have low bromine numbers. For such materials the ultra-violet method should be useful as an analysis to confirm or supplement the ASTM test. J. S.

1452. Spectrographic analysis of new and used lubricating oils. C. M. Gambrill, A. G. Gassmann, and W. R. O'Neill. *Anal. Chem.*, 1951, **23**, 1365–9.—This work was begun because accurate, rapid methods for determining the metal content of lubricating oils were needed for controlling the blending of additive oils and for examining used oils to aid engine-performance studies. Ordinary methods of chemical analysis are usually too cumbersome and tedious for this purpose, and attempts have been made to utilize the speed of spectrographic methods. A spectrographic method using the porous-cup-electrode technique is described for the determination of the additives containing barium, calcium, phosphorus, and zinc in new lubricating oils, and its variables are discussed. An overall accuracy of 10% is claimed. A second technique uses a rotating-disk electrode for the determination of lead, iron, and the additives in used oils. Results for the additives are compared with those obtained using porous-cup electrodes. Accuracies of 10% are claimed for the determination of lead and iron and the additives. Film background read adjacent to the element line used as internal standard in both techniques. J. S.

1453. Formation of engine-deposit compounds by solid-state reactions. X-ray diffraction study. F. W. Lamb and L. M. Niebylski. *Anal. Chem.*, 1951, **23**, 1388–97.—In making an X-ray-diffraction study of the inorganic lead compounds occurring in engine deposits, the importance of their formation by solid-state reactions was recognized. A study of numerous solid-state addition and replacement reactions between inorganic lead salts was undertaken. It was learned that all the compounds commonly

found may be produced as a result of additional reactions which take place in the solid state between various lead salts and lead monoxide when mixtures of these are heated at temperatures well below their melting points. The resulting or surviving products of the solid-state reactions are determined only by the temperature and by the mole ratio of the lead monoxide to the normal lead salts. A one-to-one correspondence is shown between the temp which produce specific compounds on a thermal plug in an engine and the " reaction " temp required for production of the same compounds by solid-state reaction. In a solid-state replacement reaction between a basic lead salt and a normal lead salt the reaction temp is determined not by the relative stability of the reactants, but by the temp required for the solid-state addition reaction of the released lead monoxide and the normal lead salts. The crystalline form of PbO, PbCl, Br produced from solid-state reaction between 2PbO, $PbBr_2$, and lead chloride and between 2PbO, $PbCl_2$, and lead bromide is dependent on the parent structure of the monobasic lead halide formed by the initial addition reaction between released lead monoxide and the original normal lead halide. Examples are given of increased reactivity due to the ability of metastable yellow lead monoxide to form a reactive red lead monoxide when heated in the presence of a second compound with which lead monoxide will readily form an addition product. This property is believed to be important in the mechanism of the solid-state reactions studied, and its possible relation to engine combustion phenomena is suggested. Interplanar spacing values are given for the major reflections of inorganic lead compounds commonly occurring in engine deposits. $PbO.PbBr_2$ (two forms); $PbO.PbCl_2$; PbO.Pb,Cl,Br (two forms); $2PbO.PbBr_2$; $2PbO.PbCl_2$; 2PbO.PbCl,Br; $PbO.PbSO_4$; and $4PbO.PbSO_4$.

J. S.

1454. Determination of tetra-ethyl lead in gasoline by X-ray absorption. S. W. Levine and A. H. Okamoto. *Anal. Chem.*, 1951, **23**, 1293–6.—An X-ray-absorption method for the determination of T.E.L. in gasoline has been developed to provide a faster method for plant control and other analytical needs than the existing chemical methods. Several fundamental factors not mentioned by other workers have been found to have a significant effect on accuracy, particularly when analysing gasolines of different base stock having different ratios of carbon to hydrogen and different density. Corrections must be made for absorption due to sulphur, which must be estimated by a different method. Halogenated compounds are also absorbed, but the ratio of T.E.L. to halogenated compounds is held so nearly constant in commercial T.E.L. fluid that no significant error due to variation in this ratio has been found. The T.E.L. is measured in terms of this mixture. The method developed permits the analysis of a sample in from 10 to 15 min with an accuracy of $\pm 0{\cdot}02$ ml T.E.L/gal. J. S.

1455. Determination of moisture by distillation. W. R. Fetzer. *Anal. Chem.*, 1951, **23**, 1062–9.—The distillation procedure for moisture determination measures the water as such and thereby establishes a primary or reference method for other moisture methods. The numerous applications of the distillation procedure are reviewed, some of the basic designs in apparatus which will adapt the procedure to a specific product are shown, and the best technique developed for its performance is summarized. J. S.

1456. Determination of acid number of oils and resins in aqueous medium. G. Narsimhan and S. A. Saletore. *Anal. Chem.*, 1951, **23**, 1315–17.—The acid number of oils and resins can be determined in aqueous medium, provided the hydrolysing tendency of the product is either eliminated or kept at a minimum. This has been achieved by emulsifying the sample and titrating the dilute unstabilized emulsion with aqueous alkali. This work has been extended to dark-coloured oils with satisfactory results. Results compare favourably with potentiometric methods. J. S.

1457. Determination of free sulphur in gasoline. K. Ubrig and H. Levin. *Anal. Chem.*, 1951, **23**, 1334–5.—The free sulphur content of gasoline can be estimated by measuring 100 ml of the gasoline into a 4-oz bottle followed by 2 ml of oleic acid and 3 ml of mercury. The bottle is stoppered, shaken for 5 min, and immediately compared, by transmitted light, with freshly prepared standards. Mercaptans do not interfere with the test; hydrogen sulphide if present should be removed by

shaking the sample with acid cadmium chloride solution and filtering through paper, and peroxides if present may be removed by shaking with an aqueous saturated solution of ferrous sulphate. J. S.

1458. Polarographic determination of dissolved oxygen in petroleum fractions. M. E. Hall. *Anal. Chem.*, 1951, **23**, 1382–4.—In the studies of the effect of dissolved oxygen on product quality of certain petroleum fractions, especially fractions obtained from catalytic cracking processes, a need developed for an analytical method for determining dissolved oxygen that was more rapid and simple than those described in the literature. A polarographic procedure has been applied to the determination of dissolved oxygen in gasoline base stocks, finished motor gasoline, catalytic feed stocks, and individual hydrocarbons. Tables of data show the amount of dissolved oxygen found in petroleum fractions and individual hydrocarbons. The precision was found to be ± 2 mg of oxygen per litre of hydrocarbon in the range of 20 to 40 mg of dissolved oxygen per litre. The polarographic procedure requires only 1 to 2 ml of sample, and a complete determination can be made in 10 to 15 min as compared with 2 to 3 hr by conventional methods. J. S.

1459. Determination of acetaldehyde and acetone by the iodoform reaction. Determination of 1,2-propylene glycol. S. Dal Nogare, T. C. Norris, and M. Mitchell, Jr. *Anal. Chem.*, 1951, **23**, 1473–8.—The procedure described was developed to fill the need for a method applicable to the determination of very low concentrations of acetaldehyde or acetone in solution. The method is based on the reaction of these carbonyl compounds with hypoiodite to give iodoform, which is measured spectrophotometrically at 347 mμ. Under controlled conditions acetaldehyde and acetone give reproducible iodoform yields of 58% and 108% respectively, on a mole per mole basis. By means of the procedure 0 to 0·4 mg of these compounds may be determined. In the development of the iodoform method a study was made of the reaction conditions necessary for reproducible results. The observation that iodoform in solution can be measured spectrophotometrically is a marked improvement over gravimetric and titrimetric means previously used. Specific applications of the method are reported for acetone in *cyclo*hexanol and 1 : 2-propylene glycol in ethylene glycol. J. S.

1460. New colour reaction for the detection of the methyl ketone group. J. Adachi. *Anal. Chem.*, 1951, **23**, 1491–2.—For the detection of CH_3CO—or $CH_3CH(OH)$—groups, Lieben's iodoform reaction, which relies upon smell, often gives ambiguous results. A new colour reaction has been developed and is described. When a compound that contains a methyl ketone or a methyl carbinol group is treated with alkali hypochlorite or hypobromite and the whole is heated with the addition of pyridine a carmine red or pink colour develops immediately. Quinoline and homologues of pyridine and quinoline also give the reaction, but hypoiodite is not applicable in place of hypochlorite or hypobromite. Acetone, ethanol, acetaldehyde, *iso*propyl alcohol, etc., gave the reaction. J. S.

1461. Testing used lubricating oils for *n*-pentane- and benzene-insolubles. Proposed semimicro modification of ASTM method. J. S. Wiberley, R. K. Siegfriedt, and L. J. Dipaola. *Anal. Chem.*, 1951, **23**, 1361–73.—The ASTM method for *n*-pentane- and benzene-insolubles in used lubricating oils has a number of disadvantages as a routine test, and it does not permit use of a coagulant in the determination of pentane-insolubles, so that all the insoluble matter present in a detergent-type oil may not be precipitated and measured. For these reasons a semi-micro-modification was developed. A 1-g sample of oil is used instead of a 10-g sample, and the centrifuge tubes and other apparatus are similarly smaller in size. A coagulant, *n*-butyl diethanolamine, is added in a fixed quantity in the determination of both pentane- and benzene-insolubles. This version of the method is faster, cheaper, and safer than the macro-procedure. Results obtained with coagulant are a better measure of total insolubles, and are more useful from evaluating used detergent-type oils than those obtained by the ASTM procedure. J. S.

1462. Isolation, identification and estimation of gaseous pollutants of air. Examination of Los Angeles Co., California, smog. M. Shepherd, S. M. Rock, R. Howard, and J. Stormes. *Anal. Chem.*, 1951, **23**, 1431–40.—Previous attempts to concentrate air

pollutants in a cold trap and analyse the concentrates by mass spectrometry have had disappointing results. A new method by which the air of Los Angeles Co. has been examined combines the isolation of gaseous pollutants on a filter at liquid-oxygen temp, separation of the isolated frozen concentrate by isothermal distillation or sublimation at low temp and pressures, and identification and estimation of distillate by the mass spectrometer. The method is capable of determining as little as 10^{-4} p.p.m. of some pollutants from a 100-litre sample of air; with larger samples 10^{-6} p.p.m. of some substances can be determined. The gaseous phase of the Los Angeles smog was found to be of the order of 0·5 p.p.m. of the air. About sixty chemical compounds or families of compounds were identified or tentatively identified, and the amounts of some of these were determined. It was shown that the gaseous phase of the smog was primarily a mixture of hydrocarbons, and of hydrocarbons combined with oxygen, nitrogen, and chlorine. Most important, these hydrocarbons, principally the unsaturated ones when oxidized with ozone and nitrogen dioxide in the presence of ultra-violet light, produce substances which constitute a large proportion of the smog concentrates. These oxidation products cause eye and respiratory irritation such as are produced by the real smog and smell like smog and its concentrates. Haagen-Smit has experimentally shown that these products cause the specific type of plant damage observed during actual smogs, and the present work offers substantial proof of his hydrocarbon theory of the origin of the more interesting portion of the Los Angeles smog. Unexplained residues in the mass spectra of the smog concentrate may eventually indicate the presence of other irritants. The new method may be applied to special problems in air pollution over large areas or inside industrial plants. J. S.

1463. Modern analytical distillation of crude petroleum. J. A. Lockwood, R. L. Le Tourneau, R. Matteson, and F. Sipos. *Anal. Chem.*, 1951, **23**, 1398–404.—Although many petroleum companies employ their own methods of assaying crude oil, a review of the literature reveals very little information on this subject and practically nothing involving the more modern types of distillation equipment. The new equipment described consists essentially of a spinning-band column for atmospheric and vacuum distillation, a spinning auger still (a truly novel molecular still) for fractionations that would normally be performed in a molecular still, and an all-glass equilibrium flash-vaporization unit. Typical data illustrative of the results obtained are included. A combination of these stills permits obtaining a wide variety of data to serve as a basis for the selection and evaluation of refinery processing schemes for the design or alteration of process equipment and as a basis for contractual relationships involving the sale or exchange of crude petroleum. The stills are recommended to the industry as a suitable basis for standard testing methods in these important fields. J. S.

1464. Determination of dry-sludge content of fuel oils : development of the Shell Hot Filtration Test (SHFT). W. J. Van Kerkvoort and A. J. J. Nieuwstad. *J. Inst. Petrol.*, 1951, **37**, 596–604.—A test has been developed in which the fuel oil is filtered, under pressure, through hardened filter-paper using a specially designed apparatus. This method involves a min of adsorption and flocculation of oil constituents on the filter. After filtration, filter and residue are washed with a solvent and the filter is weighed. This method has proved valuable in determining the actual dry-sludge content of all kinds of fuel oils, and it also simplifies the analysis of tank bottoms and centrifuge deposits. A. R. W. B.

1465. *n*-Heptane as a standard solvent for the asphaltene determination in asphaltic bitumen. E. Eisma and C. J. Krom. *J. Inst. Petrol.*, 1951, **37**, 582–7.—As solvents for asphaltene determinations standardized gasoline fractions have the disadvantage that within their specification limits considerable differences in composition may occur. Consequently, for one bitumen different values of the asphaltene content are found. These drawbacks may be met by the universal use of one pure solvent, for which normal heptane is suggested. A. R. W. B.

1466. The determination of the mineral constituent of coals. F. Schuster. *Brennstoff-Chem.*, 1951, **32** (23–4), 366–8.—Three methods are presented and explained in detail for determining the true mineral cont of coal. In Thiessen's method the mineral cont is determined from the composition of the incinerated ash. Holthaus's improve.

ment of this method makes allowance for the sulphate cont of the coal and the FeO cont of the ash. Schuster supports the basic principle of Thiessen's method but estimates the CO_2 cont of the coal directly, thus avoiding calculation of the carbonates from the CaO and MgO of the ash. In this simplified analytical procedure the carbonate oxides are taken together with the other constituents remaining unchanged in the incineration. The new method of calculation gives results which correspond better to the actual conditions as shown in relevant data tabulations. R. T.

1467. I.F.P. material for the detection of hydrocarbons. E. Vellinger, C. Labbe, and R. Monicard. *Rev. Inst. franç. Pétrole*, 1951, **6** (12), 403–12.—The necessary apparatus for gas extraction differs according as it is to be used for muds, cores, or cuttings. Manual methods for mud include the application of vacuum or heat. For continuous operation heating was tried and abandoned, but vacuum has been successfully applied. Hydrocarbons are easily extracted from cores and cuttings. To reduce spontaneous loss the specimens are quickly placed in special containers, and in the laboratory the gaseous contents of the container can be passed to the detector. Alternatively, a vacuum technique may be used.

In the manual detector about 50 cc of gas is injected, and the disturbance of equilibrium of the Wheatstone bridge apparatus is noted. For the examination of mud at a well an automatic recorder can be used with a continuous extractor. It is possible to inject additional air into the gas from the extractor if the hydrocarbon content is too high for the recorder. Both methane and the higher homologues are measured by alternate use of high and low temp, or by having two detectors in series.

The zeros of the instruments must be checked every 2 hr.

A portable manual detector has been used for detecting seeps.

A mobile laboratory has been used for mud logging and also for examining cores and cuttings for hydrocarbons, and this can include apparatus for resistivity measurements and also normal geological work. G. D. H.

1468. Theoretical study of the I.F.P. Wheatstone Bridge hydrocarbon detector-No. 3. R. Monicard. *Rev. Inst. franç. Pétrole*, 1951, **6** (11), 379–83.—The sensitivities of the equipment have been examined for the cases of two filaments (one in the analytical chamber) and four identical filaments (two in the analytical chamber). The gain in sensitivity in the second case is not enough to warrant the use of a greater current and four fragile filaments.

The following factors are involved in the action of the instrument: (*a*) exothermic combustion of the hydrocarbon; (*b*) cooling of the filament by the current of gas. Curves of sensitivity versus intensity of heating show a maximum, and the position of this depends on the hydrocarbons. G. D. H.

1469. Swiss standards. Sampling of liquid petroleum products. Anon. *Schweiz. Arch. Ang. Wiss. Tech.*, 1952, **18**, 68–71.—Second draft. Procedure covers gasoline, kerosine, diesel fuel, fuel oil, and lub oils. Sampling vessels illustrated include types similar to Figs 3, 5, 6 of IP 51/51, also a 1-litre Al sampling vessel, fitted with detachable wt; this vessel can also serve for transport of the sample. Two types of bottom sampler are shown. Procedure for verifying homogeneity of tank contents, checking for B.S. & W., and taking average samples is described. IP and ASTM methods are mentioned. V. B.

1470. Viscometer. Draft German standard DIN 51550. H. Umstätter. *Erdöl u. Kohle*, 1952, **5**, 104–16.—Brief comments on standard, sheets 1 to 6 of which are reproduced. Sheet 1 deals with general aspects of visc determination, definition of fundamental units and gives values of *d*, cp, cs, for water in range 0° to 100° C. Standard visc temp prescribed are 20°, 50°, 100° C and also ASTM temp of 37·8° and 98·8° C. Sheet 2 concerns the visc–temp relationship of lub oils and gives the Ubbelohde–Umstätter "viscogram." This covers visc 1 to 1,000,000 cs for temp −25° to 150° C and incorporates scales enabling following operations to be carried out: linear plotting of visc–temp; determination of Hagenbach kinetic energy correction; plotting rate of flow against shear stress to determine whether fluid under investigation exhibits Newtonian flow. Engler scale over range 1·12° to 200° E is included. Sheet 3 covers determination of V.I. according to ASTM D567–41. Sheet 4 describes the

Engler viscometer and its use (range 1·2° to 50° E extendable to 300° E with a smaller receiver, reproducibility ±3%). This instrument will no longer be recognized for referee tests. Sheet 5 deals with Vogel–Ossag instrument (kin visc range 2 to 20,000 cs with five capillaries, reproducibility ±2%) and Sheet 6 similarly covers the Ubbelohde suspended-level tube (range 1 to 10,000 cs in four tubes, reproducibility ±0·5%). V. B.

1471. Critical observations of some instruments of DIN 1995 and 1996 with appended suggestions for alteration. A. Scheuerer. *Bitumen, Teere, Asphalte, Peche*, 1951, **12** (2), 315–18.—Specs DIN 1995 and 1996 should be revised to include numerous improvements. In the R. & B. apparatus seven improvements are discussed and illustrated with sketches. In the apparatus for determining the pt of refraction the data of the spec differ between text and sketch; this is discussed fully with illustrative sketches. Determinations of the soft. pt. on the conventional apparatus are unnecessarily difficult, as shown in a sketch and explained. R. T.

1472. Revision of the specifications for the quality of cut-back-bitumen in DIN 1995. W. Becker. *Bitumen, Teere, Asphalte, Peche*, 1951, **12** (2), loose leaf.—The Committee "Cut-back-Bitumen" decided in October 1951, in Bad Durkheim, that circumstances in Germany did not call for more than one spec for cut-back bitumen. In November 1951 a draft revision of the spec was submitted to the members of the committee with a request for objections or suggestions. The draft submitted contains a suggested spec for H_2O cont, visc determination in road tar viscosimeter (STY). As abroad, the permissible range is limited from 100 to 150 s. The max cont of 10% tar oil is omitted. Other considerations are the properties of the dist residues and the extension of the uses of cut-back bitumen in Germany. R. T.

1473. New way to separate liquids. Anon. *Chem. Engng*, 1952, **59** (1), 222.—A laboratory liquid thermal-diffusion column has been operated successfully to separate compounds with identical mol. wt. or boiling point. The mixture passes through an annular space, the inner tube being at lower temp, in a similar manner to thermal diffusion of gases. The three isomers of xylene have been separated satisfactorily. Applications include separation of hydrocarbons according to structure rather than mass. D. H.

1474. Surface area of porous adsorbents. Y. Fu and F. E. Bartell. *J. Phys. & Colloid Chem.*, May 1951, **44**, 663–75.—A method for the determination of specific area of porous solids, using only adsorption data and not involving the dimensions of the adsorbates, has been presented and applied to porous glass, cellulose, ferric oxide, and silica gels. The results obtained by this method agree with those by the B.E.T. method. N. T.

1475. Measurement of specific surface areas of non-porous powders by a pressure decline liquid-permeability method. C. G. Dodd, J. W. Davis, and F. D. Pidgeon. *J. Phys. & Colloid Chem.*, May 1951, **44**, 684–98.—An analysis has been presented of the behaviour of a pressure-decline liquid-permeability apparatus, whereby the specific surface area of a packed powder sample may be calculated. Two types of apparatus to which the foregoing analysis applies are described. One modification of the basis design is especially adapted to convenient measurements of relatively high rates of flow of liquids and through beds of coarse powders having particles in the sieve size range. The other modification has been adapted for measurement with beds of fine powders in the subsieve size range. The construction and operation of the two modifications are described. Results obtained with a 70- to 100-mesh sample of glass spheres, the specific surface area of which was determined by independent precise microscopic measurements, are presented as evidence of the validity of the analysis and of the application of apparatus. Results obtained with the sample of quartz powder consisting of particles ranging from less than 1 to 7 μ in dia confirm the applicability of the method to the measurement of permeability but raise a question concerning the measurement of specific surface of powders in this size range. It is concluded that surface forces do not affect the flow of liquids through beds of particles as coarse as the 70- to 100-mesh glass spheres, but anomalies in surface-area measurements of the fine quartz powder require further investigation. N. T.

1476. Determination of oil in refinery waste waters. A benzene-extraction method. A. F. S. Musante. *Anal. Chem.*, 1951, **23**, 1374–9.—Most pollution-abatement processes relating to petroleum production and refining require determination of the oil content of waste-water samples, and the need for a rapid reliable method is evident. A wet extraction method has been devised in which the solvent is removed from the extract by distillation, thereby avoiding losses incurred when the extracted oils are recovered in evaporating-dishes on a steam-bath. Average deviations of less than 5% from known values are obtained with oils boiling above 300° F. About 1 hr is required for each determination, and the method is readily adaptable to multiple simultaneous determinations. J. S.

1477. How to test treating unit wastes. W. J. Hogan and G. E. Mapstone. *Petrol. Process.*, 1952, **7** (1), 83.—A procedure is described for determining the surface-active properties of acid-containing wastes from gasoline–sulphuric acid contacting units. It is applicable to the analysis of waste acid wash water and the neutralization caustic wash. The organic acids are determined by titration with cetyl pyridinium bromide in the presence of a chloroform layer with bromphenol-blue indicator. At the end point the blue colour is just transferred from the water into the chloroform layer. Convenient ways of reporting the results are given. D. W. F.

1478. Adaptation of a chemical balance for precision weighing. A. A. Hills. *Canad. J. Phys.*, 1951, **29**, 245.—A method is described of modifying a standard chemist's balance so that it is capable of determining the difference between wts of 200 *g* nominal value to a precision of one part in 10^7. No phase of the modification or adjustment is beyond the scope of a careful and well-trained instrument-maker, provided he is advised of the interpretation to be placed upon the peculiarities of the behaviour of the balance. S. B.

1479. Patents. Ger.P. 825,907, 22.11.51. (L. Unterstenhöfer.) Bad. Anilin- & Soda-Fabr. Apparatus for the indication of explosive gas mixtures.

Ger.P. 823,805, 31.10.51. Drägerwerk. Process for the detection of benzene vapour.

Ger.P. 823,806, 31.10.51. W. Möhle, Heidelberg. Calibrating process and apparatus for the micro gas analytical investigation after Barcroft-Warburg.

Ger.P. 823,807, 31.10.51. (K. Ackermann.) Bad-Anilin- & Soda-Fabr. Apparatus for the analysis of gas mixtures.
Brennstoff-Chem., 1951, **32** (23–4). R. T.

Engine Fuels

1480. Influence of carbon disulphide on octane number and lead susceptibility. G. E. Mapstone and J. S. Durham. *J. Inst. Petrol.*, 1951, **37**, 737–9.—The effect of carbon disulphide on the O.N. and lead susceptibility of 60 O.N. reference fuel has been determined. It has very little effect in reducing the O.N. of the sulphur-free base fuel, but a marked loss occurs with leaded samples. A. R. W. B.

1481. Fuels for use in marine auxiliary oil engines. C. D. Brewer. *Engineer*, 1952, **193**, 275. (*Summary of paper before Inst. Marine Engrs*).—It is desirable to be able to select a compromise fuel which can be used in both main and auxiliary marine oil engines to give greatest overall operating economy. Visc, provided fuel can be atomized, and ignition quality above 45 Cetane No., have little bearing on choice of fuels. Fouling characteristics are important, and proper cooling of injector to optimum temp is necessary. Tendency to foul is directly related to Conradson carbon content. Heavy fuels should be centrifuged to reduce ash content to minimum. Higher sulphur content in fuel does not necessarily create increased wear. Medium-speed and power auxiliary engines may be operated on all but heaviest of fuels without much depreciation in performance, but not without risk of increased maintenance and reduced endurance. A. C.

1482. Fuels for aviation and industrial gas turbines. M. O. Scott, R. Stansfield, and T. Tait. *J. Inst. Petrol.*, 1951, **37**, 487–509.—The relationship between production specifications for aviation turbine fuels and fuel specifications is outlined with reference to the hydrocarbon fuel properties available. It has not been found possible, on the basis of existing knowledge, to combine desirable combustion characteristics associated with the paraffins with the lowest freezing point and max economy on a volume basis, but providing requirements favour it, a wide-boiling-range type of fuel should give reasonably good combustion characteristics. The combustion problems associated with the use of residual fuels in industrial gas-turbine plants are discussed; in particular, the twin problems of ash deposition and high-temp corrosion have to be solved, it being unlikely that economic processes for the removal of vanadium and sulphur from these fuels will be found. A. R. W. B.

1483. Some considerations on the combustion in gas turbines. J. G. Dawson. *J. Inst. Petrol.*, 1951, **37**, 509–16.—Various aspects of the relationship between combustion-chamber design and fuel properties are discussed briefly. It is argued that many of the differences in the performance of fuels which are apparent in present combustion chambers can be eliminated by suitable design. In the case of the industrial combustion chamber, some insensitivity is apparent, but in the aero combustion chamber the differences in performance due to fuel characteristics, particularly physical ones, are more pronounced. A. R. W. B.

1484. Patents. U.S.P. 2,573,579 (9.11.48; 30.10.51). A. E. Lacomble, assr to Shell Development Co. Leaded gasoline containing as lead scavenger a chloro- or bromo-carbon compound containing 2 carbon atoms per molecule, *e.g.*, tetrabromo-ethylene, hexabromo- or hexachloro-ethane.

U.S.P. 2,573,933 (8.2.49; 6.11.51). L. Schmerling and J. Chenicek, assrs to Universal Oil Products Co. Olefinic gasoline containing 1-hydroxyphenyl piperidine as anti-oxidant.

U.S.P. 2,573,850 (18.3.46; 6.11.51). A. C. Korte, assr to Carter Carburetor Corp. Gum accelerating effect of copper in contact with hydrocarbon fuel is inhibited by using an alloy of 40 to 50% Cu and 60 to 50% Ag.

U.S.P. 2,575,003 (3.7.48; 13.11.51). J. B. R. Caron, F. B. Glendenning, and C. Wies, assrs to Shell Development Co. Anti-clogging concentrate for addition to fuel oil comprising 10 to 20% of iron or aluminium naphthenate, 5 to 15% of a metal salt of an organic sulphonic acid and balance of fuel oil. V. P. P.

Fr.P. 984,608, 9.7.51. A. Vloeberghs. Fuel briquettes and their production.

Fr.P. 985,877, 24.7.51. Ethyl Corporation. Improvement to anti-detonating mixtures for motor fuels.

Fr.P. 986,064, 26.7.51. Progil, S.A. Process for the briquetting of recovered carbons.
Brennstoff-Chem., 1951, **32** (23–4).

Fr.P. 976,334, 8.12.48. West's Gas Improv. Co. Mechanical gas producer.

Swiss P. 274,479, 16.6.51. Koppers Co. Production of combustible gases containing methane from finely divided solid fuels.
Brennstoff-Chem., 1952, **33** (1–2). R. T.

Lubricants

1485. Lubricating oils in the internal combustion engine. D. A. C. Dewdney, E. B. Evans, J. L. Heaton, and K. C. Hunt. *Gas Oil Pwr*, 1951, **46**, 315.—Lub-oil problems in the diesel engine are mainly concerned with deposits which consist of evaporation residues and products of cracking and incomplete combustion. Oils of high S content tend to produce more deposit, particularly in the ring grooves, than those of low S content, but such deposits are affected by the type of engine and kind of service. Reducing the jacket temp may reduce deposits, but if the temp is too low excessive wear will result. It is now usual to use detergent additives in oils of high S content.

With low-speed diesel engines the advantages of detergent additives are not so marked. In these engines the most serious lubrication problem is that of wear of cyl bore. H. C. E.

1486. 1000-mile oil change is a must. W. F. Weiland. *Petrol. Process.*, 1952, **7** (1), 69–75.—A rapid test method is described for determining the time for changing crankcase oil before corrosion of the bearings occur. It is based on the fact that progressive oil breakdown can be measured by the temp at which acid vapours are liberated, the acid-vapour temp (A.V.T.). Data on corrosion and oxidation time have been compiled from actual tests on road-engine sump oils and from a lab oxidation procedure which simulates the conditions in the crankcase. A diagram is given of the simple apparatus required for the oxidation–corrosion test. The A.V.T. of new oils is around 250° to 330° F, but incipient corrosion of both copper and aluminium has been shown to occur when the A.V.T. drops below 215° F. From road tests the A.V.T. is found to drop to this figure after 500 to 1500 miles, depending upon the oil used. Data presented include the effect of metals on A.V.T., oxidation time on A.V.T., prolonged oxidation on A.V.T. and A.V.T. and incipient corrosion. Some lub-oil additives have been shown to be highly corrosive. D. W. F.

1487. Patents. U.S.P. 2,574,994 (24.10.47; 13.11.51). D. E. Adelson, assr to Shell Development Co. Lubricant containing as stabilizer the product obtained by reacting an unsaturated $C_{\leq 12}$ cyclic ketone fraction and H_2S or NH_4HS at 15° to 100° C, followed by reaction with a phosphorus halide at 100° to 200° C in mol ratio about 1 : 4.

U.S.P. 2,573,568 (10.5.48; 30.10.51). D. Harman and R. E. Thorpe, assrs to Shell Development Co. Lubricant containing a dialkyl trihalo-alkane phosphonate as E.P. agent.

U.S.P. 2,573,650 (22.3.49; 30.10.51). W. H. Peterson, assr to Shell Development Co. Inorganic gel greases are water-proofed by incorporating a non-metallic hydrophobic aliphatic hydroxy compound containing ≤ 8 carbon atoms, *e.g.*, 12-hydroxy stearic acid; 1 : 10-decamethylene glycol; glycerol monostearate.

B.P. 659,082 (14.6.48; 17.10.51). Monsanto Chemical Co. Polystyrene is reacted in the presence of a Friedel–Crafts catalyst with a $C_{\leq 8}$ aliphatic monocarboxylic acid in mole ratio 1 : ≥ 1. Product has use as V.I. improver and pour-point depressant, as a tackifier in greases, in hot melt coatings, etc. V. P. P.

Fr.P. 988,905, 3.9.51. Standard-Kuhlmann. Improvement of raw materials for the synthesis of lubricating and insulating oils.
Brennstoff-Chem., 1951, **32** (23–4). R. T.

Bitumen, Asphalt, and Tar

1488. Pilot plant investigations on cold water separation of bitumen from Alberta bituminous sands. L. E. Djingheuzian. *Canad. Min. metall. Bull.*, Jan. 1952, **45**, 2–15.—Plant, procedure, and the standard ore-dressing machinery employed in the cold-water separation of bitumen from bituminous sands are described, and results of operations are given and discussed. Using Bitumount diluent (a heavier-than-kerosine distillate obtained from the Bitumount Plant, sp. gr. 0·88) with small amounts of soda ash and a wetting agent, a recovery of 95% of bitumen was obtained from the Horse River bituminous sands. Soda ash must be used to ensure good recovery, and an optimum pH of just over 9 is required. The optimum range of temp was found to be between 73° and 81° F. Best recoveries are obtained when the mineral matter in the sands is reduced in the pebble-mill from 5 to 7% −200 mesh, to 11 to 15% −200 mesh. Increase in clay content affected thickener recoveries adversely; there appears to be an optimum content which will assist in effecting the highest overall recoveries. W. H. C.

1489. Report on bituminous sands of Alberta. H. I. Waterman and A. Brakel. *Ingenieur*, 22.2.52, **64** (8), M19.—It is considered that the hot-water-extraction process for recovering the bituminous material is not normally an economic one, and that it is preferable to treat the deposits without making a separation of the sand

and bitumen. (The bitumen content of the sand amounts to 16% by wt.) The possible application of the Ljunstrom method of *in situ* electric heating, whereby the oil could be vaporized or cracked, is mentioned. The bituminous deposits could be compounded into materials serviceable for road construction, or in large-scale hydraulic engineering. Tables are included of ultimate analyses of the bituminous extract before and after hydrogenation, which latter product was almost completely saturated. R. R.

1490. Binder proportioning for bituminous fine material surfacings. G. Herion. *Bitumen, Teere, Asphalte, Peche*, 1951, **12** (2), 297–301.—The most familiar theories and methods of construction apply to standard conditions regarding materials and climate, but examination of a group classification of such methods explains their unsuitability for general application and indicates the necessity for a simplified procedure. Such a procedure based on expert knowledge and experience must be applicable to any available stone and given binder, as far as possible on the building site. Requirements are knowledge of the type of binder and its visc; for the mineral, the type, sieve analysis, cavities, and grain form are necessary. Fundamental data are discussed, and the procedure for the determination of the correct binder addition is presented graphically. Thirty-four literature references. R. T.

1491. Patents. U.S.P. 2,574,930 (24.3.47; 13.11.51). R. G. Mitchell, S. A. Hunn, R. G. Green, and W. L. Ghijsen, assrs to Shell Development Co. Alkaline asphalt-in-water emulsion containing 40 to 60 wt-% asphalt, 0·2 to 0·5% alkali-metal aluminate, 1 to 2% casein, emulsifying amounts of a water-soluble soap-type emulsifier, and sufficient H_2O_2 and CH_3CHO to produce a pH 3 to 7 when reacted together. V. P. P.

Ger.P. 823,457, 22.3.51. J. Oberbach, Bad. Godesberg/Rhein. Procedure for the surface treatment of streets, tracks, etc. (Addition to 801,014, 2.11.48.)

Ger.P. 823,150, 12.4.51. C. van Staalen, Soesterberg (Holland). Process and plant for producing an asphalt- or cement-concrete mixture, especially for road construction.
Bitumen, Teere, Asphalte, Peche, 1951, **12** (2).

Ger.P. 823,740, 31.10.51. (E. Moehrle and H. Franck.) Ges. f. Teerverwertung. Procedure for the improvement of tar oils.
Brennstoff-Chem., 1951, **32** (23–4). R. T.

Special Hydrocarbon Products

1492. Propylene petrochemicals. V. C. Irvine. *Petrol. Process.*, 1952, **7** (1), 46–8.—The commercially most important propylene primary derivatives are shown in diagrammatic form, of which *iso*propyl alcohol and alkyl chloride are considered in more detail. *Iso*propyl alcohol, formed by hydration of propylene, is important for conversion to acetone, which is itself a raw material for diacetone alcohol, hexylene glycol, methyl methacrylate, and methyl *iso*butyl ketone. Hot chlorination of propylene yields alkyl alcohol, the main uses of which are for the production of synthetic glycerine and resins. Several other propylene derivatives are briefly mentioned. D. W. F.

1493. Patents. U.S.P. 2,573,294 (2.6.47; 30.10.51). J. Ackerman and C. W. Moberly, assrs to Phillips Petroleum Co. Stabilizing hydrocarbons with the reaction product of a phenol and a Sn″, Cr″, Co″, Cu′, or Fe″ salt of a $C_{<16}$ fatty acid.

U.S.P. 2,573,882–3 (12.4.47; 6.11.51). G. W. Waters, assr to Shell Development Co. Composition (acid val 3 to 15) for use in coating (ferrous) metals with tin or lead consisting of min oil and (*a*) a hydrogenated fatty oil, or hydrogenated residuum or distillate fractions thereof, or (*b*) partially hydrogenated fish-oil distillates, and an arylamine as stabilizer. (U.S.P. 2,573,940 claims a composition (acid val 4 to 10) consisting of slop wax free from aromatics, partially hydrogenated fish-oil distillate, phenyl α-naphthylamine, and optionally dimethyl silcone to aid draining.)

U.S.P. 2,573,422 (24.3.47; 30.10.51). J. J. Fish, assr to Sun Chemical Corp. Composition forming stable aq emulsions which give glossy films on drying are obtained

by catalytically oxidizing at 275° to 400° F a hydrocarbon wax containing minor proportions of chlorinated paraffin and a drying or semi-drying oil (which may be a blown oil). In U.S.P. 2,573,423 a similar mixture, but containing also an olefin polymer, is oxidized.

U.S.P. 2,574,528 (6.3.47; 13.11.51). G. E. F. Brewer, assr to Gage Products Co. An electrically neutral solution comprising 10 parts by vol of a non-polar liquid (naphtha, toluene, benzene, mineral spirits, CCl_4) which generates static electricity at an interface with a solid with which it is in mobile contact, and 1·5 to 10 parts by vol of hexylene glycol.

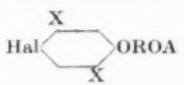
U.S.P. 2,575,098 (4.12.46; 13.11.51). C. C. Crawford and L. L. Jaquier, assrs to Phillips Petroleum Co. Insecticidal composition comprising branched-chain paraffins *A* boiling in range 360° to 410° F and a soluble insecticide. It is claimed that *A* increases the toxicity of the insecticide, while the usual kerosine solvent does not.

U.S.P. 2,573,953 (1.11.48; 6.11.51). J. P. Buckmann, assr to Union Oil Co. of California. Pesticidal compound containing 0·5 to 15 wt-% halogen and 5 to 30 wt-% S is prepared by reacting a halogenated pet distillate containing 1 to 4 halogen atoms per mol with an alkali-metal polysulphide or mixture of alkali-metal sulphides with sulphur at 50° to 200° C.

U.S.P. 2,573,862 (16.7.49; 6.11.51). A. Minich and M. Nowak, assrs to Nuodex Products Co. Pesticidal composition comprising a zinc salt of petroleum sulphonic acids of mol. wt. 375 to 500 in mineral spirits.

U.S.P. 2,576,946 (19.11.49; 30.10.51). M. Paulshock, assr to E.I. du Pont de Nemours & Co. Composition for controlling mites and aphids comprising a 3-hydroxy-1 : 4-naphthoquinone substituted in the 2-position by a C_{6-15} alkyl, *cyclo*alkyl, or *cyclo*hexylalkyl radical, or a salt thereof.

U.S.P. 2,573,769 (4.1.49; 6.11.51). J. A. Lambrech, assr to Union Carbide and Carbon Corp. Herbicidal compound of formula



wherein Hal = Cl or Br; X = H, Cl or Br; R = $-CH_2.CH_2-$ or $-CH_2CH_2-O-CH_2CH_2-$ and A is a sulphuric or phosphoric acid group neutralized with an amine, Na, K, Ca, Ba, Mg, or NH_4.

U.S.P. 2,574,526 (16.8.49; 13.11.51). G. C. Borden, assr to Riegel Paper Corp. An anti-fungus wrapping-paper having an inner coating of a dialkyl dichlorosuccinate and a grease-resistant, wax-immiscible filmogen, and an outer coating of wax.

V. P. P.

Ger.P. 825,394, 15.11.51. (O. Bretschneider.) Deutsche Gold- u. Silber Scheidearmt. Method for the production of hydrocyanic acid.

Ger.P. 825,252, 15.11.51. (P. H. De Bruijn.) Directie van de Staatsmijnen. Process for the separate recovery of anthracene, phenanthrene, and carbazole.

Ger.P. 824,490, 8.11.51. (H. Müller and W. Oversohl.) Aglukon-Ges., Düsseldorf. Method for the production of hexachloro*cyclo*hexane.

Ger.P. 825,546, 15.11.51. (J. Nowotny.) Farbenfabriken Bayer. Process for the separation of mixtures of *cyclo*hexanol and *cyclo*hexanone.

Ger.P. 826,294, 22.11.51. (H. F. Rickert, E. Stein, and O. Bayer.) Farbenfabriken Bayer. Process for the production of *cyclo*hexene.

Ger.P. 825,262, 15.11.51. (P. H. De Bruijn.) Directie van de Staatsmijnen. Method for the preparation of carbazole.

Ger.P. 825,415, 15.11.51. (P. H. De Bruijn.) Directie van de Staatsmijnen. Method for the production of resorcinol.

Brennstoff-Chem., 1951, **32** (23–4). R. T.

Derived Chemical Products

1494. Patents. U.S.P. 2,574,481 (17.8.49; 13.11.51). J. C. Hillyer, assr to Phillips Petroleum Co. Producing 4-vinyl-1-*cyclo*hexene and 1 : 3-butadiene of high purity by heating 1 : 5-*cyclo*-octadiene at 650° to 1000° F.

U.S.P. 2,573,947 (1.7.49; 6.11.51). E. R. Bell, F. F. Rust, and W. E. Vaughan, assrs to Shell Development Co. Preparation of alkyl hydroperoxides by reacting H_2O_2 with an alkylating agent in aq solution in presence of an acid catalyst and extracting the product as rapidly as formed with a water-immiscible solvent.

U.S.P. 2,574,832 (5.4.47; 13.11.51). M. S. Kharasch, assr to United States Rubber Co. Production of adducts of 1-alkenes with compounds in which the group CCl_2Br is linked to H, alkyl, bromine, or bromo-alkyl in presence of free radicals produced by action of actinic light or from a diacyl peroxide.

U.S.P. 2,573,973 (30.9.50; 6.11.51). H. L. Johnson and A. P. Stuart, assrs to Sun Oil Co. 1 : 2 : 3 : 4-Tetrachlorobutane is reacted with alkali-metal thiocyanate at 50° to 150° C in an inert solvent in presence of Cu powder or an alkali-metal bromide or iodide.

U.S.P. 2,574,480 (26.11.48; 13.11.51). J. C. Hillyer and J. F. Wilson, assrs to Phillips Petroleum Co. Reacting an acetylenic hydrocarbon with HF in ratio 1 : 1 to 1 : 4 at 350° to 750° F in presence of a catalyst comprising 70 to 95 wt-% alumina and 5 to 30 wt-% ZnF_2.

U.S.P. 2,574,511–12 (18.3.50; 13.11.51). W. G. Toland, assr to California Research Corp. In oxidation of naphthalene to phthalic anhydride at 800° to 1200° F in presence of a vanadia catalyst, temp profile of catalyst bed is smoothed by passing SO_2 therethrough. No. 2,574,512 relates to a similar process for oxidation of *o*-dialkyl benzenes.

U.S.P. 2,574,884 (28.4.49; 13.11.51). C. W. Mertz, H. W. Cutcher, and J. A. McBride, assrs to Phillips Petroleum Co. Oxidation of *tert*-alkyl ($C_{>4}$) mercaptans to sulphides in presence of a catalyst comprising alumina and vanadia, magnetic iron oxide, or chromia at 150° to 450° F.

U.S.P. 2,573,674 (26.7.50; 6.11.51). C. E. Adams and W. A. Proell, assrs to Standard Oil Co. Production of sulphonyl halides by reacting a non-tertiary saturated hydrocarbon disulphide *A* at from −40° C to +20° C with chlorine in amount to leave at least 5% of unconverted *A*, and then oxidizing the reaction mixture with $O_2 + NO_2$.

U.S.P. 2,573,730 (15.3.48; 6.11.51). L. C. Rubin, assr to M.W. Kellogg Co. Excess C_{10-18} normal olefins is reacted with 80% aq H_2SO_4 at 0° to −20° C, and the reaction mixture passed to a second zone, where excess of this acid is added, the reaction mixture being recycled to the first zone from which the reaction product is withdrawn. V. P. P.

Coal, Shale, and Peat

1495. Studies of low-grade Indian coals. S. S. Ghosh *et al.* *Brennstoff-Chem.*, 1951, **32** (23–4), 368–74.—Pt 1 of this article presents a systematic study of some Indian coals to obtain complete details of their composition and temp of incipient decomp. Seven high-ash, low-grade coals from the almost inexhaustible Iharia field and two low-ash coals with a high volatile cont from the Ranigunj field for comparison, were investigated for their suitability for complete gasification, hydrogenation, or low-temp carbonization. The analyses and temp of incipient decomp show clearly that the coals of these two more important Indian coalfields differ widely in age. The conception that they belong to the true bituminous coals is incorrect. The coals of the Ranigunj field obviously belong to the series of sub-bituminous coals, and are of more recent origin. Highly carbonized coals, such as those of the Iharia field, are preferred for complete gasification. Such coals are unsuitable for hydrogenation or low-temp carbonization. Coals of the Ranigunj field are more suitable for these purposes. In Pt 2 carbonization experiments with the same coals and the reactivity of two typical low-temp cokes will be dealt with. R. T.

1496. Patents. Ger.P. 825,988, 22.11.51. (E. Kuhl, W. Sehrt, and R. Sehrt.) Saarl. Brennst.-Techn. G.m.b.H. Heating-surface low-temperature-carbonization furnace.

Ger.P. 824,486, 8.11.51. (E. Kuhl.) Brennst.-Techn. G.m.b.H. Procedure and plant for low-temp carbonization with coupled firing.

Ger.P. 823,634, 31.10.51. H. Schmalfeldt, Castrop-Rauxel. Process for the gasification of coal dust in suspension.

Ger.P. 823,635, 31.10.51. H. Schmalfeldt, Castrop-Rauxel. Method for producing synthesis gas free from hydrocarbons by gasification of coal dust in suspension.

Ger.P. 826,745, 29.11.51. (H. Just.) Ruhrgas A.-G. Process for the elimination or reduction of the capacity of coals for caking.

Ger.P. 829,588, 27.12.51. (E. Kuhl.) Saarl. Brennst-Techn. G.m.b.H. Vertical oven for the coking of coals.

Ger.P. 830,043, 27.12.51. (H. J. Challis.) I.C.I. Process for introducing fine powdered, solid materials into reaction vessels, for example, carbonizing chambers.

Ger.P. 828,398, 13.12.51. K. Krafft, Witten (Ruhr). Process for producing stable coarse-lump low-temp coke from bitumen-rich brown coal.

Ger.P. 828,693, 20.12.51. (W. Kieckebusch, Detmold.) Procedure and plant for dehydrating peat and similar strongly water-retaining materials.
Brennstoff-Chem., 1952, **33** (1–2).

Fr.P. 986,623, 2.8.51. No patentee given. Distillation furnace for fuels such as peats and lignites.
Brennstoff-Chem., 1951, **32** (23–4). R. T.

Miscellaneous Products

1497. Aerosol insecticides—their evaluation against house flies, cockroaches. Pt I. A. C. Miller, A. Mallis, and R. V. Sharpless. *Soap Sanitary Chem.*, Feb. 1952, **28** (2), 151.—New physical and biological procedures are needed for aerosols. The Tentative NAIDM (CSMA) Aerosol Test Method for Flying Insects 1949–50 is in use with the Tentative Official Test Aerosol (TOTA) as standard. This article discusses various factors in establishing a method—use of free-flying or caged flies, dosage, exposure period, TOTA, test chambers, manner of releasing aerosol, size of test populations, etc., reporting results as knockdown, knockdown mortality, or total mortality. In this part the variation in the average dosage is studied, and was found not to be of great consequence against house flies. N. W. G.

1498. German cockroach control (ratios of piperonyl butoxide and pyrethrins). E. J. Incho. *Soap Sanitary Chem.*, Feb. 1952, **28** (2), 142.—The increased demand for pyrethrum insecticides for home use (with its wide margin of safety for warm-blooded mammals) has focused attention on synergists. With house flies, pyrethrins–piperonyl butoxide give a critical ratio. Using German cockroaches it has been found that, with ratios from 1 : 10 to 1 : 5 as oil-based sprays and 1 : 10 in emulsion form, a product about one and a half times as effective as pyrethrins alone is given. N. W. G.

1499. Disinfectant test methods. A. R. Cade. *Soap Sanitary Chem.*, Feb. 1952, **28** (2), 144.—A report of co-operative tests on methods for the evaluation of germicidal efficiency of cresylics and quaternaries. Three methods were included—A.O.A.C. method, Stuart Carrier or Ring test, and Klarmann-Wright Semi-micro method—in a series of tests covering two half-year periods with variations in organisms (*S. typhosa* and *M. aurens*) and different materials as antidotes in sub-culture media. The conclusions of the tests, using six laboratories, were that the semi-micro method is preferred—the A.O.A.C. method being found unsatisfactory for quaternary ammonium compounds. A number of proprietary antidotes were tested in the sub-culture media with little or no preference between them. The semi-micro method is also suitable for testing cresylic-type disinfectants, but no antidotes are recommended, as no suitable ones are known. N. W. G.

1500. Patents. U.S.P. 2,574,987 (10.3.50; 13.11.51). T. H. Shelley, assr to B. F. Goodrich Co. Polymers of vinyl or vinylidene chloride stabilized to heat and light with an imide containing the grouping R–CO–NH–CO–R, where R = hydrocarbon group.

B.P. 661,367 (11.9.47; 21.11.51). Boake, Roberts & Co. Ltd., M. F. Carroll, and W. G. Wearmouth. As plasticizer for PVC is used an ester of an aliphatic or aromatic polybasic carboxylic acid with an alcohol having a number a of C atoms <8 and an alcohol boiling $\leq 160°$ C, having a number b of C atoms ≤ 8, the alcohols being selected so that $\frac{na + mb}{n + m}$ is >3 but <10, where n and m are the numbers of each esterified alcohol group in the ester. V. P. P.

Corrosion

1501. The corrosion of buried metals. Anon. *Petroleum*, Mar. 1952, **15** (3), 66–70.—A summary, with discussion, of the papers presented at a symposium on the corrosion of buried metals which was held by the Iron and Steel Institute in conjunction with the British Iron and Steel Research Association and the Corrosion Group of the Society of Chemical Industry. The papers read were: (1) Tests on the corrosion of buried iron and steel pipes (J. C. Hudson and C. P. Acock); (2) Investigation on underground corrosion (K. R. Butlin, W. H. J. Vernon, and L. S. Whiskin); (3) Cathodic protection of buried metal structures (R. de Brouwer); (4) Cathodic protection (K. A. Spencer); (5) Corrosion of buried copper and ferrous strip in natural and salted soils (Brit. Elec. and Allied Ind. Research Association); (6) Tests on the corrosion of buried aluminium, copper, and lead (P. T. Gilbert and F. C. Porter).
R. E. P.

1502. Literature survey on corrosion in neutral unaerated oil well brines. H. R. Copson. *Corrosion*, 1951, **7** (4), 123–7.—Corrosion of steels is observed, and may be expected, in well waters of low pH or containing oxygen. Corrosion also occurs in neutral oxygen-free waters, and is difficult to explain. Depolarization may be caused by nitrates, by anaerobic bacteria, or by sulphur compounds, or corrosion may arise from Fe–FeS galvanic cells, but the last is improbable in the absence of oxygen. It is concluded that much more investigation is required. In a general discussion the possible protective role of oil films on the steel is mentioned, as well as the effects of erosion, stress, and corrosion fatigue. The most successful inhibitor is formaldehyde. A list of forty-six references is given. K. G. B.

1503. Corrosion fundamentals in field application. A. Chatenever. *World Oil*, 1.7.51, **133** (1), 194.—A general discussion on corrosion, the relation between the underlying theory, and the practical problem. A general appreciation of basic facts is essential to progessive developments in the prevention of corrosion. A. J. H.

1504. Corrosion inhibition in gas condensate wells by intermittent injection of alkaline solutions. C. C. Nathan. *Corrosion*, 1951, **7** (11), 397–9.—Corrosion of high-pressure gas-condensate wells on the Gulf Coast is attributed to condensed water containing carbon dioxide and low-mol.-wt. fatty acids. Where possible, continuous injection of alkaline solutions, mainly via the casing/tubing annulus, has been successful in preventing the corrosion. If this annulus is closed by mud, intermittent injection is possible by pumping soda solution down the well. The protection thus afforded decreases as the solution is scrubbed from the walls by the gas, and it therefore lasts longer at low production rates. The quantity of alkali added is insufficient to neutralize all the acid in the well, and its function seems to be to coat the well surfaces with a layer of alkaline water. K. G. B.

1505. Applications of organic corrosion inhibitors in the petroleum industry. C. M. Blair. *Corrosion*, 1951, **7** (6), 189–95.—The corrosion of oil- and gas-well equipment by acidic materials in the oil or brine may be minimized by the use of small quantities of organic inhibitors. These are usually complex polar materials, such as naphthenic acids, amines, alcohols, etc., and they are available as liquids or solids. Methods of

charging inhibitors to wells are described, and examples given of successful applications. They appear to function by adsorption on the metal, and on this basis the dependence of corrosion rate on inhibitor concentration should be $RC = K$ (R = corrosion rate, C = concentration, K = constant). In two practical examples the relation was $RC^n = K$, where $n = 1{\cdot}6$ approx. K. G. B.

1506. Prediction of corrosion in oil and gas wells. D. A. Shock and J. D. Sudbury. *World Oil*, Oct. 1951, **133** (5), 180. (*Spring Mtng Pacific Coast Dist., API Los Angeles, May* 11, 1951.)—Corrosion in wells, other than those producing sour crudes, received little attention before 1945, but the noticeable corrosion in condensate wells revealed the necessity for its study. The primary contribution is in the water phase, the distribution of which differs in oil well to that in gas-condensate well. In the former the concentration of water does not vary much with depth, but the water in the liquid phase increases in concentration as the condensate fluid approaches the surface; the corrosive water is almost in equilibrium with the steel when produced at the surface.

Carbon dioxide and hydrogen sulphide both add to the corrosive action of water when soluble in it. It has been shown that the distribution of solubility of carbon dioxide in water agrees closely with that of the degree of corrosion in particular wells. Although the complete corrosive mechanism in the field is not due to a single agent, laboratory investigations have to be conducted under controlled conditions. The experimental procedure is described also for the effect of carbon dioxide and acetic acid together. Certain compounds of the polar group have been known to reduce appreciably the corrosiveness of certain waters.

The significance and validity of tests on corrosive waters are discussed in detail, and an introduction given to the prediction of corrosive action of well fluids; general rules are summarized. Eighteen references. A. J. H.

1507. Bacterial casing corrosion in the Ventura field. K. Doig and A. Wachter. *Corrosion*, 1951, **7** (7), 212–24.—Withdrawal of well casing in the Ventura Avenue field, California, disclosed that the numerous failures due to external corrosion were caused by anaerobic sulphate-reducing bacteria. The corrosion was confined to wells drilled using mud of low pH (8·5), which provides a suitable medium for sulphate-reducers at the casing surface. The prevention of corrosion in existing wells is most difficult, but future wells will be drilled with mud of high pH (about 11). Laboratory tests have shown that bacterial activity ceases in muds of high pH in a few weeks. K. G. B.

1508. High pressure sweet oil well corrosion. H. L. Bilhartz. *Corrosion*, 1951, **7** (8), 256–64.—A statistical survey has been made of the corrosion experienced in high-pressure sweet oil wells in southeast Louisiana. The attack takes the form of pitting, and failure occurs, on the average, in two to four years. Barium sulphate scale may also be deposited when water is present, but water is not necessary for the pitting to occur. Its intensity depends on the amount of carbon dioxide present, and the wells affected also have a high organic acid content. The trouble is worse in wells with greater bottom-hole temp and pressures and having greater depth. Phenolic-resin coatings are resistant to corrosion, giving only occasional pits, and with better deposition technique they may offer complete protection. 9% nickel steel is very resistant, but is expensive; nickel plating is also suggested. Inhibitors have not been used successfully, owing to the difficulty of introducing them into the wells. K. G. B.

1509. Economics of rectifier installation for cathodic protection of a bare pipeline. D. C. Glass. *Corrosion*, 1951, **7** (10), 322–6.—A description of the installation and operation of cathodic protection on a bare 10-inch crude-oil pipeline in the Texas–Gulf Coast area. After ten years' experience it is concluded that such an installation is economically feasible. K. G. B.

1510. Potential measurements for determining cathodic protection requirements. S. P. Ewing. *Corrosion*, 1951, **7** (12), 410–17.—Sets of six 10-inch lengths of steel pipe were buried in three different locations, and one set was submerged in water. Different potentials relative to a common anode were applied to the members of each set using a battery and a potentiometer system. As far as possible the open-circuit pipe/soil

potentials, as measured with a calomel half-cell, were controlled by adjusting the currents, and the weight changes of the samples were determined after seventy to eighty days. It was concluded that the open-circuit pipe/soil potential required for cathodic protection depends upon the environment, and may be less negative than the normally accepted limit of −0·85 V measured with the copper/copper sulphate half-cell. Also, in some cases it is desirable to use a high initial current to form a coating, which subsequently allows a substantial reduction in current without impairing the protection. K. G. B.

1511. Control of sour crude corrosion in Kansas production operations. L. C. Case. *Corrosion*, 1951, **7** (11), 390–6.—The corrosion mainly affects the interior of well tubing and the sucker rods, and is due not to the oil phase but to brine containing hydrogen sulphide and carbon dioxide; oxygen is normally absent. Failure may occur in severely corrosive wells in 4 to 7 months. The first successful protective measure was inhibition by formaldehyde, and this has been followed by a number of oil-soluble organic inhibitors which operate by adsorption on the metal surfaces. Attempts to use more resistant materials and to neutralize the brine chemically were unsuccessful. K. G. B.

1512. A proposed standard method for measuring the electrical resistance of pipeline coatings. W. F. Rogers, B. H. Davies, L. Sheppard, L. G. Sharpe, E. R. Allen, D. Bond, and P. T. Miller. *Corrosion*, 1951, **7** (7), 245–51.—The procedure has been developed by the National Association of Corrosion Engineers Technical Practices Committee 17, and is known as the Current-Voltage Method. Current is made to flow from a steel ground-bed to the pipeline using a portable generator. The current flowing along the pipe is measured at intervals of, say, 5000 ft, and current flow into the pipe obtained by difference. Pipe-soil potentials are measured with a copper sulphate half-cell. The coating resistance is then calculable from the changes in current and pipe–soil potential obtained when the generator is switched on and off. K. G. B.

1513. A proposed alternative method for measuring the electrical resistance of pipeline coatings. J. K. Ballou, R. P. Howell, J. W. Liljeberg, and P. F. Offermann. *Corrosion*, 1951, **7** (12), 438–40.—The general equation is derived relating the voltage of a pipeline at any point and the current flowing along it to its resistance and its attenuation constant, which is the square root of the ratio of pipe resistance per unit length to the coating resistance per unit length. Given pipeline current and voltage measurements, this equation may be solved graphically to determine the attenuation constant, and hence the coating resistance. Allowance can be made for soil resistance. K. G. B.

1514. Corrosion and scale control. E. N. Jones. *World Oil*, Aug. 1951, **133** (3), 204.—Acids have been used successfully for the removal of scale. The methods of application in the field are described, with reference to scale on liners and screens and the removal of muds from the well. Chemical treatment has been found to remove and inhibit further scale formation. A. J. H.

1515. Engineering inspection for corrosion control. F. A. Upson. *Oil Gas J.*, 17.3.52, **50** (45), 227.—The organization of an inspection group at the Whiting refinery of Standard Oil Co. and maintenance inspection, inspecting methods, and use of records are described. G. A. C.

1516. Corrosion and its control. M. E. Parker. *Oil Gas J.*, 3.3.52, **50** (43), 93.—The use of protective metallic coatings are described in Pt 47 of this series. Four general methods of applying metal as a coating include dipping in molten metal, electroplating, spraying of molten metal, and deposition of weld metal. Spraying and welding processes have outstanding advantages, including applicability to structures too large or too complex to be dipped or plated. G. A. C.

1517. Some corrosion problems in petroleum refineries. J. F. Mason, Jr. *Petrol. Engr*, Feb. 1952, **24** (2), C10–18. (*ASME Mtng, Tulsa, Sept.* 1951.)—Fifteen varied

problems of refinery equipment corrosion have been investigated using a spool-type specimen holder placed in the desired location. The results are discussed at length.
E. K. J.

1518. Corrosion, and its control in chemical plant. C. W. Day. *Chem. Engng*, 1952, **59**, 155–9. (*Nat. Assoc. Corrosion Engrs, U.S.A.* 1951.)—The programme of a corrosion-control department should have flexibility to test mainly specific problems rather than routine tests. Regular inspections are essential, however, in order to predict failure, and to justify the cost of the department.

The chief sources of corrosion and some more unusual cases are described. D. H.

1519. Thermofor catalytic cracking gas plant corrosion survey. C. A. Murray. *Corrosion*, 1951, **7** (3), 98–108.—Serious corrosion has been experienced in the gas plant of the Pure Oil Co. catalytic cracker at Smith's Bluff, Texas. In coolers and heat exchangers, steel tubes initially installed failed mainly owing to attack from the water side, and Admiralty brass replacements suffered corrosion from the process side. The latter corrosion was worst where large amounts of aqueous condensate were present containing high concentrations of ammonia and hydrogen sulphide, for example, in the depropanizer overhead condenser and depropanizer charge-bottoms exchanger. Steel tubes in depentanizer and debutanizer reboilers were corroded by water-soluble organic acids assumed to arise from the dissociation by heating of ammonium salts, and this corrosion was aggravated by iron sulphide sludge from other parts of the plant. To reduce gas-plant corrosion the quantity of water present should be reduced to a minimum, and chemical neutralization of the small amount of water remaining may then be practicable. K. G. B.

1520. Magnolia reduces furnace corrosion in polyformer. J. J. Baker. *Oil Gas J.*, 17.3.52, **50** (45), 306.—Corrosion of equipment has been reduced, and maintenance costs lowered, with increase of stream time, by installation of higher-alloy furnace tubes and header material in polyform furnaces at the Beaumont refinery.

Six figures illustrate the article. G. A. C.

1521. Furnace tube-end corrosion. F. C. Braun. *Oil Gas J.*, 17.3.52, **50** (45), 285.—Localized corrosion occurring at furnace-end tubes has been successfully minimized by Gulf Oil Corp. by employing a method for rolling in close-tolerance machined upset tubes, accurately expanded.

Figures show joints with various tubes, and a tube-end machining specification is given. G. A. C.

1522. How to control internal corrosion of crude still condenser. M. J. Wilcox and F. M. Watkins. *Oil Gas J.*, 17.3.52, **50** (45), 290.—The use of inhibitors has considerably reduced corrosion in condenser systems at Sinclair Refining Co.'s Hartford plant. The inhibitor is used at rate of 1 gal/24 hr, and adsorbs on iron and iron-oxides as a monomolecular film. G. A. C.

1523. Salt-water corrosion in refinery cooling equipment. B. M. Beildeck and O. F. Noss. *Oil Gas J.*, 17.3.52, **50** (45), 296.—Costs of salt-water corrosion at Los Angeles refinery of Union Oil Co. are outlined and mechanism of the attack discussed.

Reduction of outlet temp of the warm-salt-water exchangers to max of 120° F has reduced corrosion; and to a lesser extent so has backflushing, efficient skimmers, and flow contol by outlet valves. G. A. C.

1524. Cities Service tackles brackish-cooling water corrosion. J. J. Picarazzi. *Oil Gas J.*, 17.3.52, **50** (45), 271.—Source of water is Calcasieu River, and analysis of water is given. Large solid objects are screened out, and intermittent chlorination practised.

Bottom line, tubular condenser, and cooler corrosion is described, and tube sheet metal of corrosion-resistant type used in replacements.

Velocity has been found to be a critical factor, high velocities leading to impingement attack, and low ones cause concentration-cell corrosion.

Nine figures depict various types of attack. G. A. C.

1525. Low-temperature corrosion in a crude-distillation tower. T. N. Grisnold. *Oil Gas J.*, 17.3.52, **50** (45), 247.—Low-temperature corrosion, if not combated, can be more costly than many high-temperature types.

Ammonia injection and crude desalting, carefully operated, will reduce heavy maintenance expenditures.

Monel metal is most economic material for internal use, and austentitic stainless metals types 304 and 316 have shown negligible losses in coupon tests. G. A. C.

1526. Corrosion in hydrocarbon processing. J. C. Reidel. *Oil Gas J.*, 17.3.52, **50** (45), 203.—Practical answers dealing with engineering corrosion problems, such as corrosion types, causes and prevention, materials used to combat corrosion, corrosion testing, cathodic protection of condensers and heat exchangers are given. G. A. C.

1527. How to combat corrosion in processing oil and gas. M. E. Parker. *Oil Gas J.*, 17.3.52, **50** (45), 236.—This is a specially illustrated report covering causes of corrosion and methods of prevention. Basic and special types of corrosion, losses, weapons, corrodents, detection and diagnosis, design, testing methods, control of unanticipated corrosion are included in subjects discussed. G. A. C.

1528. General petroleum licks erosion problem in T.C.C. catalyst-handling lines. D. H. Stormont. *Oil Gas J.*, 17.3.52, **30** (45), 266.—The catalyst lines at the Torrance Calif, refinery needed replacing every twelve months. By inserting pockets at all places where a line changed direction, erosion problem was solved. Lining of kilns protected the insulation, and rebushing elevator chains resulted in increased life. G. A. C.

1529. Applications of cathodic protection to control refinery corrosion. V. W. Hatchett. *Oil Gas J.*, 17.3.52, **50** (45), 256.—Practical suggestions are made on the adaptation of old and proved techniques to new uses, and nine case histories given. The sacrificial anode procedure in obtaining cathodic protection is commonly used. The economics of cathodic protection are briefly discussed. G. A. C.

1530. Case histories of corrosion problems and use of protective coatings in their solution. W. B. Cook. *Oil Gas J.*, 17.3.52, **50** (45), 313.—Corrosion histories at Port Arthur refinery of Gulf Oil Corp are given, relative to interior tank corrosion. Five-coat vinyl system, bottom rust corrosion, plastic-lined valves are among subjects discussed. G. A. C.

1531. Stainless steels for the bottoms of tanks containing sour crude oil. C. P. Larrabee and W. F. Rogers. *Corrosion*, 1951, **7** (8), 276–8.—The corrosion of the bottoms of steel storage tanks containing sour crude oils is due to sulphide-bearing salt water. A series of stainless steels have been tested for this duty by immersion for a year in the aqueous phase of a crude-oil–water separator. Ferritic stainless steels suffered very heavy attack, but austenitic steels were not corroded, except for slight pitting of Type 347 steel. Experience has shown that molybdenum-bearing austenitic steels are less susceptible to pitting, and the most suitable materials for tank bottoms are probably Types 316 and 317. K. G. B.

1532. Phenolic cements. R. B. Seymour and R. H. Steiner. *Chem. Engng*, 1952, **59** (1), 264.—Corrosion resistance with 180 solids, liquids, and gases of acidic, basic, and salty and organic natures is given in graphical form. D. H.

1533. Patents. U.S.P. 2,573,878 (26.4.48; 6.11.51). K. F. Schiermeier and H. A. Poitz, assrs to Shell Development Co. Rust-inhibiting composition consisting essentially of 35 to 45% asphaltic bitumen, 5 to 20% oxidized non-aromatic petroleum oil–wax mixture and 1 to 5% metal salt of an organic cyclic (naphthenic) or sulphonic acid, diluted with a hydrocarbon boiling below the lub-oil range.

U.S.P. 2,574,955 (14.7.48; 13.11.51). J. W. Bishop, assr to Tide Water Associated Oil Co. For use in preventing rust, a salt of an acid ester of a phosphorus acid containing C_{4-30} hydrocarbon ester residue, and a mono-amine containing an esterified alkylol group, if desired in association with the free acid ester. U.S.P.

2,574,954—as a rust-inhibiting composition, a hydrocarbon vehicle, and 0·01 to 20 wt-% of an addition product of acid lauryl phosphate and a tertiary ethanolamine stearate or oleate ester. In U.S.P. 2,574,956 is used a salt of an acid phosphate ester containing a C_{8-12} alkyl group and β-(N-diethyl)aminoethyl stearate or oleate, and sodium salts of pet mahogany acids. V. P. P.

Engines and Automotive Equipment

1534. British gas turbine work in 1951. Anon. *Gas Oil Pwr*, 1952, **47**, 3–6.—A summary of gas-turbine installations now installed or under project in Great Britain, classified under the maker, user, power, and state of development.

Progress with different fuels is also reported. A combustion chamber now in operation has an efficiency of 90% with peat as fuel, and a 500-h.p. Parsons experimental turbine is now running on pulverized coal using a straight-through tubular combustion chamber. English Electric are building a turbine capable of operating on methane either alone or mixed with another fuel. The problem of corrosion caused by vanadium and sodium oxides in the ash from heavy oil fuels may be reduced or overcome by the use of suitable additives in the fuels. H. C. E.

1535. Foreign gas turbine work in 1951. Anon. *Gas Oil Pwr*, 1952, **47**, 30–4.—A summary of gas-turbine installations now being developed outside Great Britain, classified under the maker, user and location, power, and stage of development. Installations in the U.S.A. and France are described in greater detail than the remainder.

A brief description is given of some trials with pulverized coal, both in the U.S.A. and in Switzerland.

Comparing British progress (Abs. 1534) with that elsewhere, it appears that whilst there are fewer gas turbines actually running in Britain, development work in that country and in America is similar, and both are superior to the Swiss work.

H. C. E.

1536. Blackburn-Turbomeca gas turbines. Anon. *Gas Oil Pwr*, 1952, **47**, 43–5.—These six small units of French design have outputs up to *ca* 350 b.h.p., and can be used as air compressors, helicopter power drives, pump drives, standby electricity generators, starting power for larger gas turbines, etc. Their fuel consumption (*ca* 1 lb/b.h.p.hr.) is high, but this is offset by their high power/wt ratio, portability, and fuel tolerance.

When used as air compressors delivering air at 50 p.s.i., two-thirds of the air passes through the combustion chamber and the remainder is output. Fuel is sprayed radially into the combustion chamber from the main shaft. H. C. E.

1537. The design of combustion chambers for the coal-fired gas turbine. T. F. Hurley. *J. Inst. Petrol.*, 1951, **37**, 517–34.—The design of combustion chambers for coal-fired gas turbines is discussed in relation to development work being carried on with various units in the U.S.A. and Europe. A. R. W. B.

1538. High-speed high-power railway oil engines. Anon. *Gas Oil Pwr*, 1952, **47**, 12–14.—This range of engines, constructed by Maybach Motorenbau, is built in three pressure-charged and four naturally aspirated models to provide a power range of 300 to 1200 b.h.p. Some of these are available as horizontal or as vertical units. In each the cyls have the same dimensions of 185 mm bore and 200 mm stroke, and units of four, six, eight, and twelve cyl are available. They operate at 1600 or 1700 r.p.m.

The fuel consumption is 0·365 and 0·385 lb/b.h.p.hr. at 1200 r.p.m. and full speed respectively.

The piston-head is of steel and the body of cast iron, and the pistons have a separate oil-circuit with ample provision for cooling. As a result of very efficient cooling, the clearances are finer than is usual in high-speed engines. Three inlet and three exhaust valves are supplied per cyl. Each cyl-head also bears an injector and pump of special design to deliver the large amount of fuel required per stroke.

The electric starting system is so designed that the first operation is to start an electric lub-oil pump, and when oil pressure has been built up a relay permits the engine to be started. H. C. E.

1539. Ford diesel engine. Anon. *Gas Oil Pwr*, 1952, **47**, 15.—This four-cyl engine has cyl of dimensions 100 mm bore and 115 mm stroke, giving a swept volume of 220 cu. in. and a rated output of 40·5 b.h.p. at 1600 r.p.m. The C.R. is 16 : 1.

Fuel is injected through a four-hole nozzle into a recess at the top of the Al piston which forms the combustion chamber. Pressure lubrication by a gear-type pump supplies oil to the main and big-end bearings; the pistons, gudgeon-pins, and cyl bores are splash lubricated. A separate supply at lower pressure lubricates the timing gears. H. C. E.

1540. Clark-Sulzer [diesel] units for Australia. Anon. *Gas Oil Pwr*, 1952, **47**, 26–9.—The TPF48 engine has eight cyl of bore and stroke 480 and 700 mm respectively, and has an output of 2800 b.h.p. at 250 r.p.m. with a b.m.e.p. of 71 p.s.i. The pistons have forged-steel heads and cast-iron skirts, and are cooled by forced lubrication through telescopic tubes. Oil then flows to the sump via the main bearings. It is continuously filtered and cooled before delivery under pressure to the various points.

A fuel-injection pump is provided for each cyl. Scavenging air is supplied by a double-acting pump driven off the main shaft.

The engine is directly coupled to an alternator having an output of 2280 kVA. H. C. E.

1541. Sentinel vertical twin [diesel engine]. Anon. *Gas Oil Pwr*, 1952, **47**, 37.—The two cyl of this unit have stroke and bore of $4\frac{3}{4}$ inches and $5\frac{1}{4}$ inches respectively, and the engine develops 30 b.h.p. at 1500 r.p.m. equivalent to a b.m.e.p. of 85 p.s.i. The C.R. is 16 : 1.

Fuel is injected through C.A.V. multi-hole injectors into toroidal cavities in the crowns of the Al-alloy pistons, which carry three compression and two slotted scraper rings. A gear oil-pump delivers oil at pressure to the main bearings, camshaft, and valve gear. Cooling water is circulated by a centrifugal pump.

The fuel consumption is 0·42 lb/b.h.p.hr., and the dry wt of the engine is 1000 lb. H. C. E.

1542. Admiralty standard range 1 engine. Anon. *Gas Oil Pwr*, 1952, **47**, 46.—These units are manufactured with six or eight cyl (in line) and twelve or sixteen cyl (in Vee form). The cyl dimensions are $9\frac{3}{4}$-inches bore and $10\frac{1}{2}$-inches stroke, and the engines operate at a max of 1000 r.p.m., giving outputs of 125 b.h.p/cyl when pressure charged and 87·5 b.h.p. with atmospheric induction.

The features of the engines include the use of an all-welded frame, open combustion chambers, four-valve cyl-heads, and Cr-plated cyl liners. Lubrication is on the dry-sump principle, and hydraulic governors are fitted. H. C. E.

1543. Nordberg three-cylinder four-stroke engine. Anon. *Gas Oil Pwr*, 1952, **47**, 42.—This 4FS3 vertical engine has cyl of bore $4\frac{1}{2}$ inches and stroke $5\frac{1}{4}$ inches and develops 30 to 45 b.h.p. at 1200 to 1800 r.p.m. It is designed for stationary applications, and has a radiator cooling system with the cooling water thermostatically controlled. Electric- or hand-starting equipment is provided. H. C. E.

1544. Gas engine-driven compressors for refinery service. Anon. *Gas Oil Pwr*, 1952, **47**, 41.—These Cooper–Bessemer sets, built by Harland and Wolff, consist of a V-type gas engine combined with a horizontal compressor. The two-stroke engines are built in units of four-, six, eight, or ten cyl, giving outputs of 250 to 2500 b.h.p. at speeds from 400 to 250 r.p.m. The engines can be arranged to run on a wide variety of gases. H. C. E.

1545. Ruston dual fuel engines. Anon. *Gas Oil Pwr*, 1952, **47**, 10.—These are vertical four-stroke engines with cyl sizes either 8 inches bore and $10\frac{1}{4}$ inches stroke, or $10\frac{1}{4}$ inches bore and $14\frac{1}{2}$ inches stroke, and are available in units of four, five, or six cyl.

The engine is started on diesel fuel, and the movement of a single lever switches in the gas supply and reduces the diesel fuel to 10% of the normal charge. The gas and air flows can be regulated independently. Details of the engine construction are given.

The engines are designed to operate on a wide range of oil fuels, and on natural, town, sewage, or producer gas of calorific value not less than 135 B.Th.U.s per cu. ft.
H. C. E.

1546. Patent. U.S.P. 2,573,694 (30.7.46; 6.11.51). E. A. De Zubay and R. A. Sforzini, assrs to Westinghouse Electric Corp. Combustion chamber with stepped-wall construction.
V. P. P.

Safety Precautions

1547. Control and extinguishment of oil tank fires by agitation. Several Authors. *Petrol. Process.*, 1952, **7** (1), 54–6; *Refiner*, 1952, **32** (1), 77–82; *World Petrol.*, Feb. 1952, **23** (2), 44–5; *Oil Forum*, Feb. 1952, **6** (2), 42–3.—Full-scale tests are described in which oil-tank fires were controlled and extinguished by injecting air at the base of the tank. Fires with liquids having flash points above atmospheric temperature could be completely extinguished, injection at the centre of the tank being most effective. Fires with low-flash-point oils were brought under control and easily extinguished with foam.
A. R. H.

1548. Safety rules for pipeliners. B. G. Pierce. *World Oil*, Aug. 1951, **133** (3), 239.—Increased mileage of pipeline communication has necessarily resulted in a large increase in man-power in this particular field. The various types of work are considered, giving principal safety regulations.
A. J. H.

1549. Patent. Ger.P. 825,987, 22.11.51. (A. Hillenbrand.) Heinrich Koppers. Safety device to prevent the rise of the gas pressure in the heating unit of a regeneratively heated furnace.
Brennstoff-Chem., 1951, **32** (23–4).
R. T.

Miscellaneous

1550. North American operating refineries. Anon. *Oil Gas J.*, 17.3.52, **50** (45), 322.—Location, capacities, types of processes, and summary of plants in Canada and Mexico are listed. Shutdown plants also shown.
G. A. C.

1551. Refining capacity in nation continues to gain. R. B. Tuttle. *Oil Gas J.*, 17.3.52, **50** (45), 334.—Survey shows thirty major expansion projects, involving input capacity increases. Capacity rating, status, completion date, and contractors are shown.
G. A. C.

1552. The training of a technologist—The Redwood Lecture. F. H. Garner. *J. Inst. Petrol.*, 1951, **37**, 663–77.—The bias towards classical education of the Universities in former ages is discussed. Earlier ideas on technological training are quoted to indicate the persisting spirit of reform which was bent upon bringing university education into line with the conditions and thought of each succeeding age. Present methods of education of technologists at universities are discussed, and the important work which can be done in graduate schools is pointed out.
A. R. W. B.

1553. A pattern of the oil industry. Anon. *Petroleum*, Mar. 1952, **15** (3), 71.—A summary of the 7th Henry Spurrier Memorial Lecture given in London by C. T. Brunner, which dealt with the special characteristics of the oil industry and its organization, with particular reference to British participation.
R. E. P.

1554. Synthetic liquid fuels—when and how? E. Ayres. *Petrol. Process.*, 1952, **7** (1), 41–4.—Some problems confronting the establishment of a synthetic-liquid-fuel industry are mentioned. Some speculations are made regarding the state of the energy industry as a whole at the end of the century. The integration of coal, petroleum, and electric-power technologies is foreseen, involving a greatly increased coal output, with pipeline transportation, for the production of tar, aromatics, and a

fine char for synthetic fuel via Fischer–Tropsch process, but mainly for electric power. The tar would be the main source of liquid fuels.

The onset of the synthetic-fuel development is largely dependent upon the course of production of world petroleum. U.S. and world petroleum production and demands are estimated for the next 100 and 300 years respectively by means of an extrapolation technique which the author attempts to justify. By this means the peak of world production is estimated to occur around 1985, and 1960 for the U.S., with demand greatly in excess of production. The indications from this are that oil-shale exploitation should be mature by 1965 with the large-scale development of low-temperature carbonization of coal under way by 1980 to provide, with petroleum, the bulk of the liquid fuel and power. D. W. F.

1555. New type forms provide closer control of refining costs. V. L. Elliot. *Petrol. Process.*, 1952, **7** (1), 62–4. (*Financial and Accounting Group session, Ann. Mtng. API, Chicago, Nov.* 5–8.)—A new type of accounting form is described as now adopted by Atlantic Refining Co. for recording costs for control purposes. Two forms are shown, one providing for an analysis of variations in costs contains such data as utilities costs, service functions, overhead accounts, and total operating costs for each refinery. The second, for top management only, gives a comparison of expected and actual cost by the month, and also provides for analysis of variations in major expense items. D. W. F.

1556. Identify chrome steels quickly. H. M. Randall. *Petrol. Process.*, 1952, **7** (1), 60–1.—A simple and rapid field test is reported for identifying corrosion—resistant alloy steels according to chromium content. Three nitric acid solutions of different concentrations are used to determine normal Cr content in steels ranging from 2 to 12% to within $\pm 1\%$. The reactions to the spot test for the three solutions on steels with up to 12% Cr are listed. D. W. F.

ADDITIONS TO THE LIBRARY.

Petroleum Measurement Manual. London: The Institute of Petroleum, 1952. Pp. 227 + viii. 30*s* (to IP members 25*s*), post free.

During the past four years, the Measurement and Sampling Sub-Committee of the IP has devoted much time and thought to the methods by which accurate measurement of bulk quantities of liquid petroleum products can be achieved. The result of their work is now available in this book of 227 pages, which in its six parts lays down instructions and details of apparatus for tank calibration, oil gauging, sampling for quantitative purposes, temperature measurement, specific gravity and density measurement, and calculation of oil quantities. The committee is confident that the adoption throughout the industry of its recommended procedures will result in close agreement nationally and internationally in calculated quantities.

Mass Spectrometry. London: The Institute of Petroleum, 1952. Pp. 205. 30*s* (to IP members 25*s*), post free.

Report of the April 1950 conference organized by the IP Mass Spectrometry Panel. Includes fourteen papers, discussion, and a bibliography of nearly 700 references.

THE INSTITUTE OF PETROLEUM

NOTICES, MAY, 1952

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The object of this information is to assist the Council in grading the candidate according to the class of membership.

The name of candidates' proposers and seconders are given in parentheses.

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BRYAN, Warren Bradley, trainee, Regent Oil Co. Ltd. (*J. R. Taylor ; T. F. McGuinness.*)

COOPER, John Godfrey, petroleum engineer, Kuwait Oil Co. Ltd. (*G. A. Hogg ; R. M. S. Owen.*)

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DEBENHAM, Arthur Douglas, buyer, Messrs. E. B. Badger & Sons (G.B.) Ltd. (*E. A. Elledge ; A. C. Morris.*)

FANSHAWE, Hew Dalrymple, assistant petroleum engineer, Kuwait Oil Co. Ltd. (*G. A. Hogg ; R. M. S. Owen.*)

FISH, Frank Herbert, production controller, Kuwait Oil Co. Ltd. (*E. Boaden, W. C. Buie.*)

FURLONG, David Barry, superintendent (Personnel), Anglo-Iranian Oil Co. Ltd. (*B. D. Cauthrey ; K. S. Ross.*)

GORDON, John Kenneth, tool pusher, Apex (Trinidad) Oilfields Ltd. (*L. A. Bushe ; M. A. Rust.*)

GRIFFITHS, Henry Walter Lindsay, student apprentice (mechanical engineer), Anglo-Iranian Oil Co. Ltd. (*P. F. Ellis ; E. J. Horley.*)

HARRISON, Sidney, deputy chief fire officer, Kuwait Oil Co. Ltd. (*W. C. Buie ; E. Boaden.*)

HUMPHRIES, Eric Norton, refinery plant operator, Anglo-Iranian Oil Co. Ltd. (*W. Miller ; G. Sell.*)

HYMERS, James, petroleum engineer, Kuwait Oil Co. Ltd. (*G. A. Hogg ; R. M. S. Owen.*)

IRON, Henry John, engineer representative, Messrs. C. C. Wakefield & Co. Ltd. (*L. G. Packham; W. F. Line.*)

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KEEP, Desmond Sidney George, general manager, Messrs. Gaunt & Hickman Ltd. (*G. H. Thornley; S. E. Holmes.*)

LAMB, John, section leader, Anglo-Iranian Oil Co. Ltd. (*R. E. Adlington; D. A. Fox.*)

MARSHALL, Peter A., cost accountant, Kuwait Oil Co. Ltd. (*G. A. Hogg; R. M. S. Owen.*)

MOORE, Norman Frederick Alexander, co-ordination sales promotion, Esso Petroleum Co. Ltd. (*E. W. Hardiman; C. Chilvers.*)

MOSS, Stephen, chief fire officer, Kuwait Oil Co. Ltd. (*W. C. Buie; G. A. Hogg.*)

NAUGHTON, Dennis George, assistant fire officer, Kuwait Oil Co. Ltd. (*G. A. Hogg; R. M. S. Owen.*)

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OSBORN, Eric, senior foreman (M. T. Workshops), Kuwait Oil Co. Ltd. (*E. Boaden.*)

PHILLIPS, Derek John, tool pusher, Apex Trinidad Oilfields Ltd. (*L. A. Bushe; M. A. Rust.*)

POGSON, Thomas William Stewart, assistant administration officer, Kuwait Oil Co. Ltd. (*G. A. Hogg; R. M. S. Owen.*)

PYWELL, Frederick Richard, branch operations officer, Shell-Mex & B.P. Ltd. (*E. Huntley; A. Moon.*)

QUAYLE, Harold Dallas Michael, senior accountant, Kuwait Oil Co. Ltd. (*G. A. Hogg; R.M.S. Owen.*)

RAJABATHAR, G., junior scientific assistant, Ministry of Defence (Government of India). (*E. Venkatachalam; C. R. Krishnamurthi.*)

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SEARSON, Anthony Hugh, process engineer, Esso Petroleum Co. Ltd. (*I. McCallum; A. W. Pearce.*)

TAUPIN, Pierre Jean, patents—products specifications, Standard Francaise des Petroles. (*E. B. Evans; A. Osborn.*)

TURNER, Thomas Edward, assistant marine superintendent, Kuwait Oil Co. Ltd. (*D. S. Curtis; E. Boaden.*)

WINTER, Robert Archibald Duncan, senior quantity surveyor, Kuwait Oil Co. Ltd. (*E. Boaden; R. M. S. Owen.*)

Transfers.

DOUGARY, James McCulloch, chemical engineer, Kuwait Oil Co. Ltd. (*C. A. P. Southwell; L. T. Jordan*) (*Member to Fellow.*)

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THOMAS, Eric Marsden, assistant process operator, Anglo-Iranian Oil Co. Ltd. (*P. F. Ellis; E. J. Horley*) (*Student to Associate Fellow.*)

WHITEHEAD, Robert Christopher, geologist, B.H.P. Co. Ltd. (*F. G. Hunter; G. H. Titchmarsh*) (*Student to Associate Fellow.*)

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BADDELEY, D. I.
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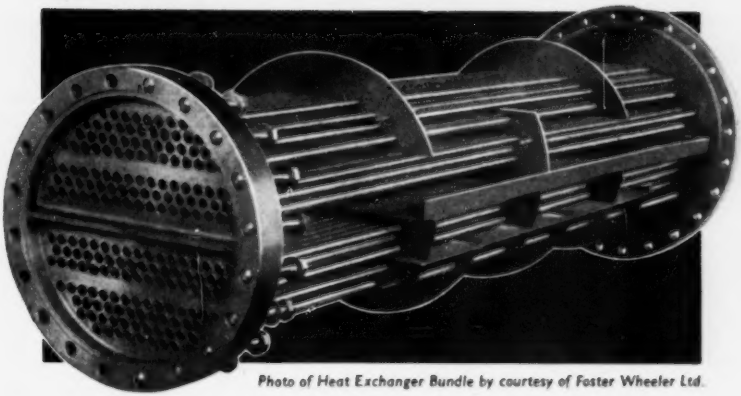

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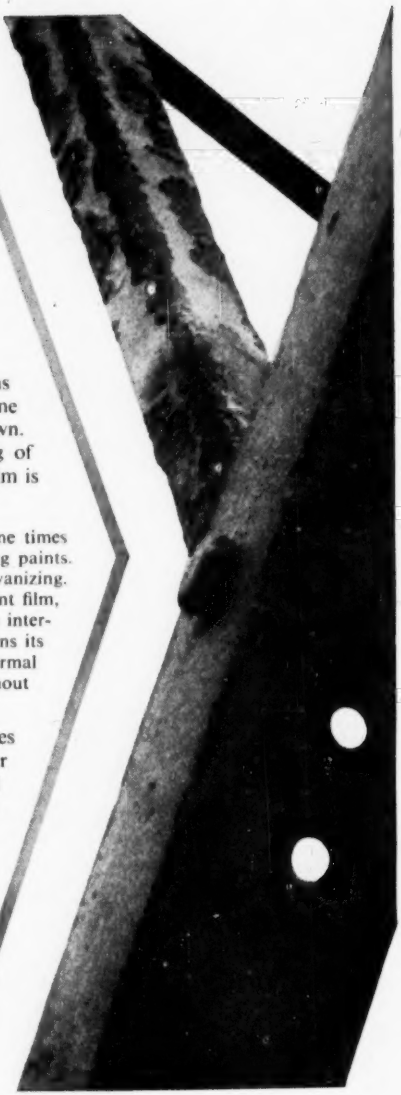

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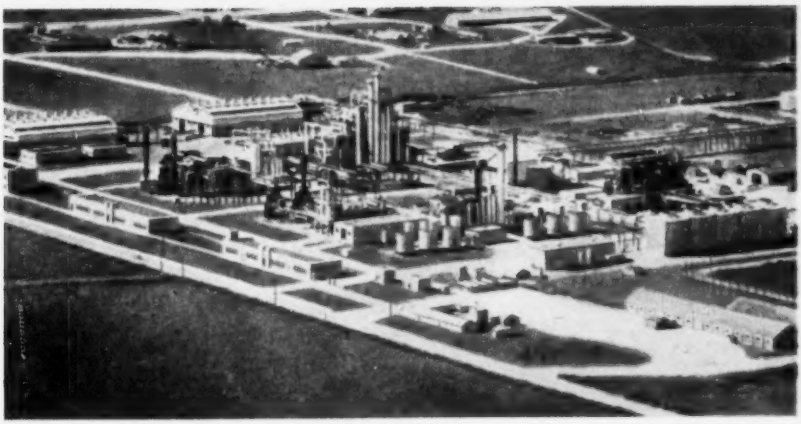

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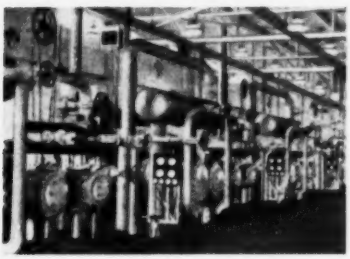

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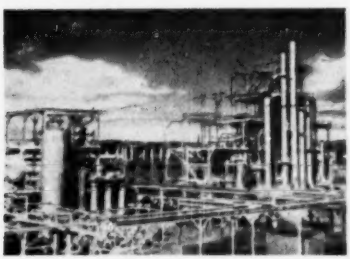

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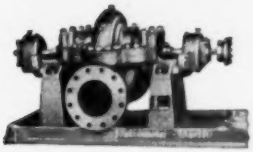

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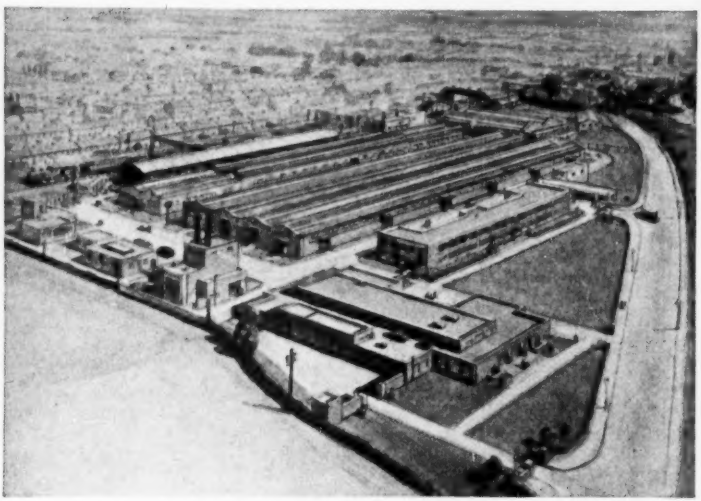

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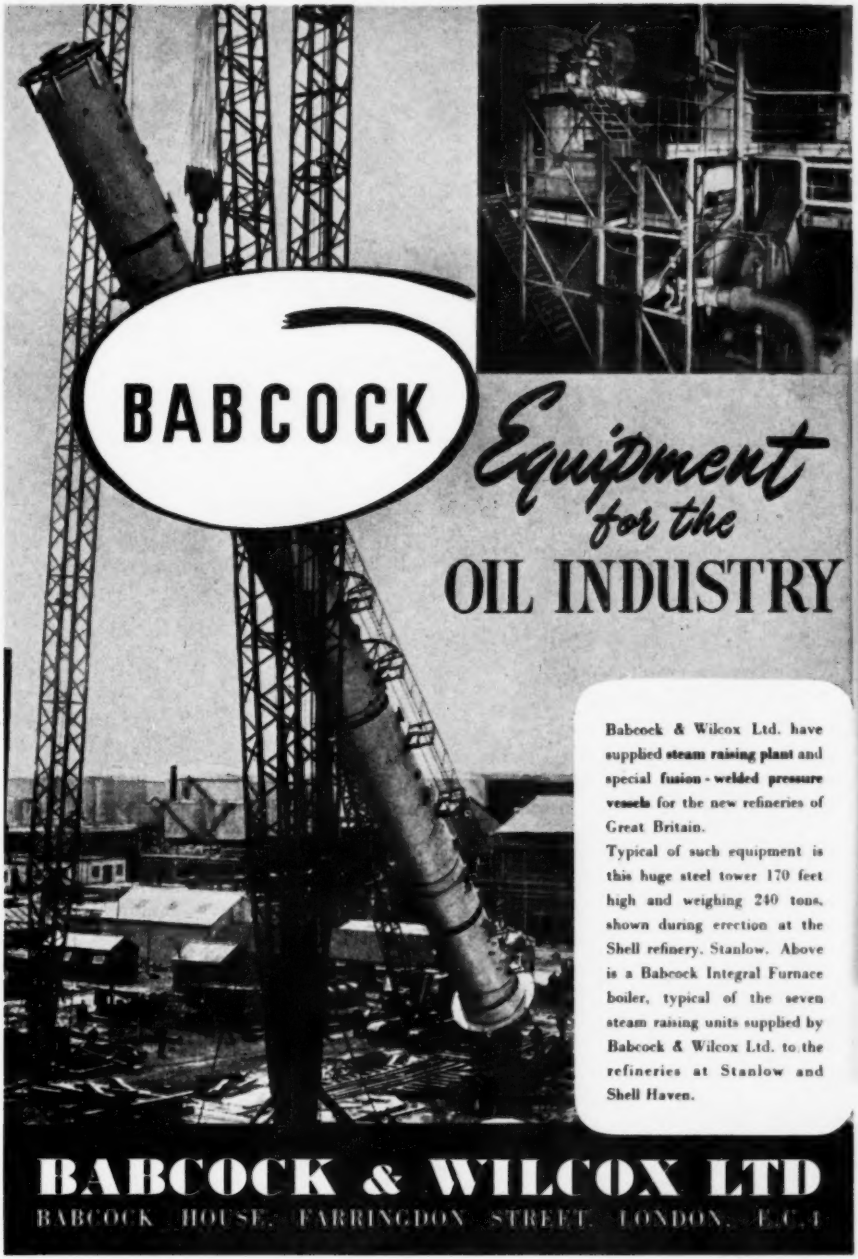
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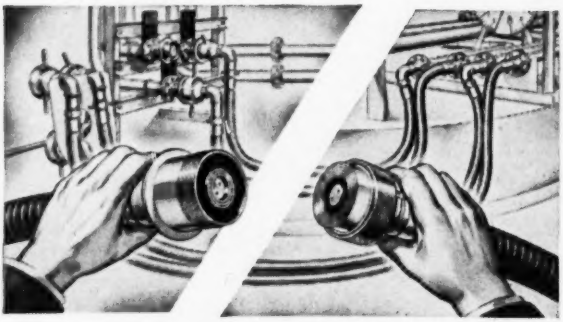

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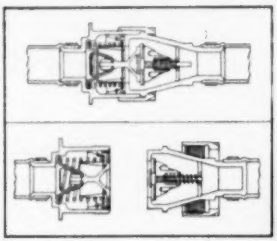

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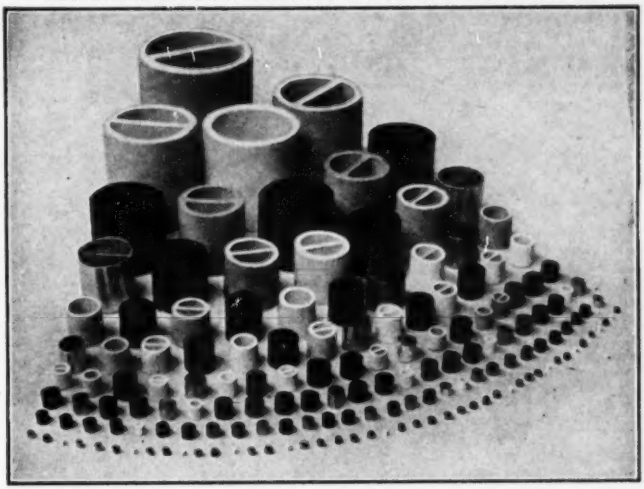

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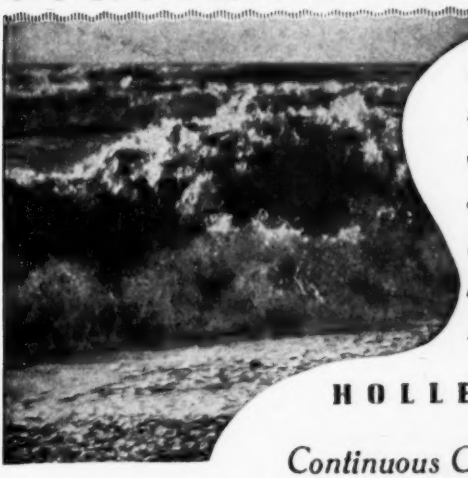

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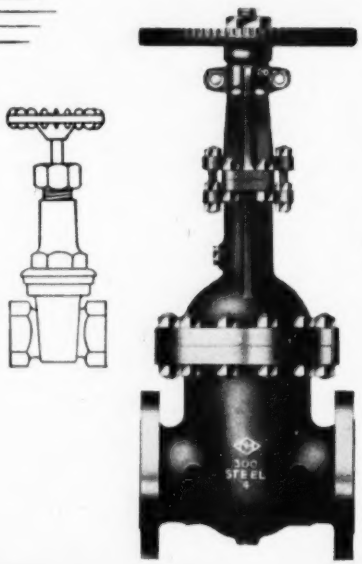

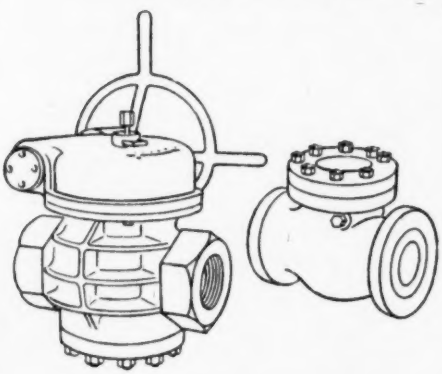

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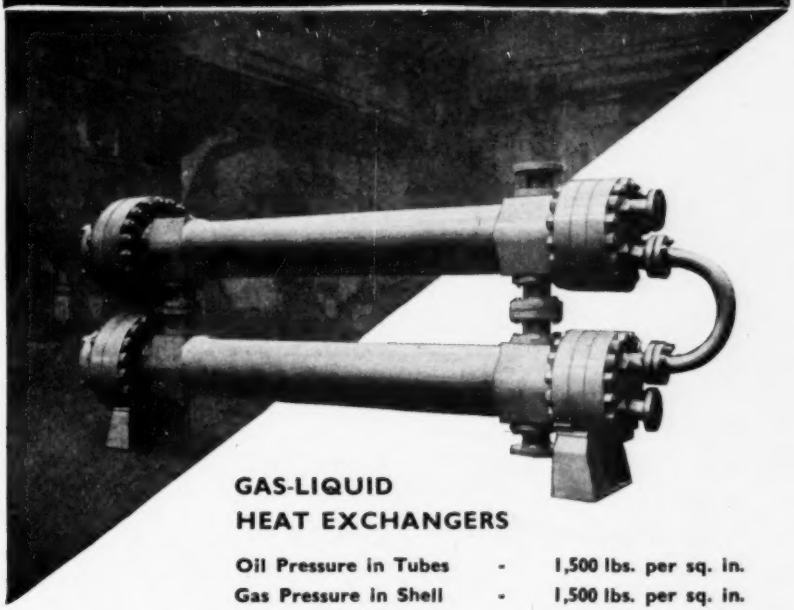

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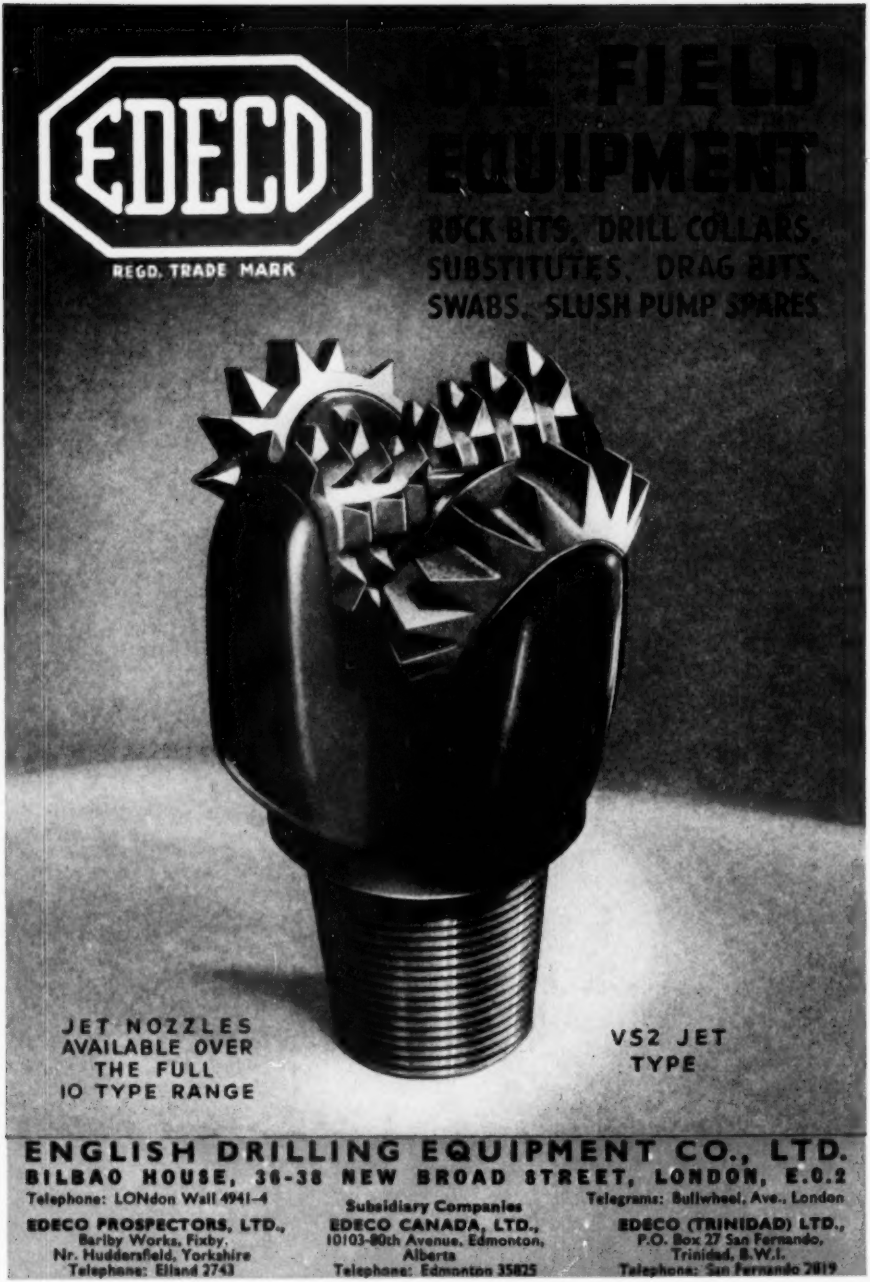
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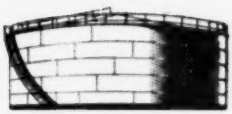

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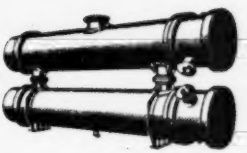

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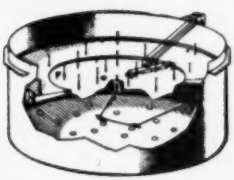

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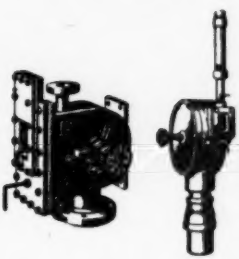

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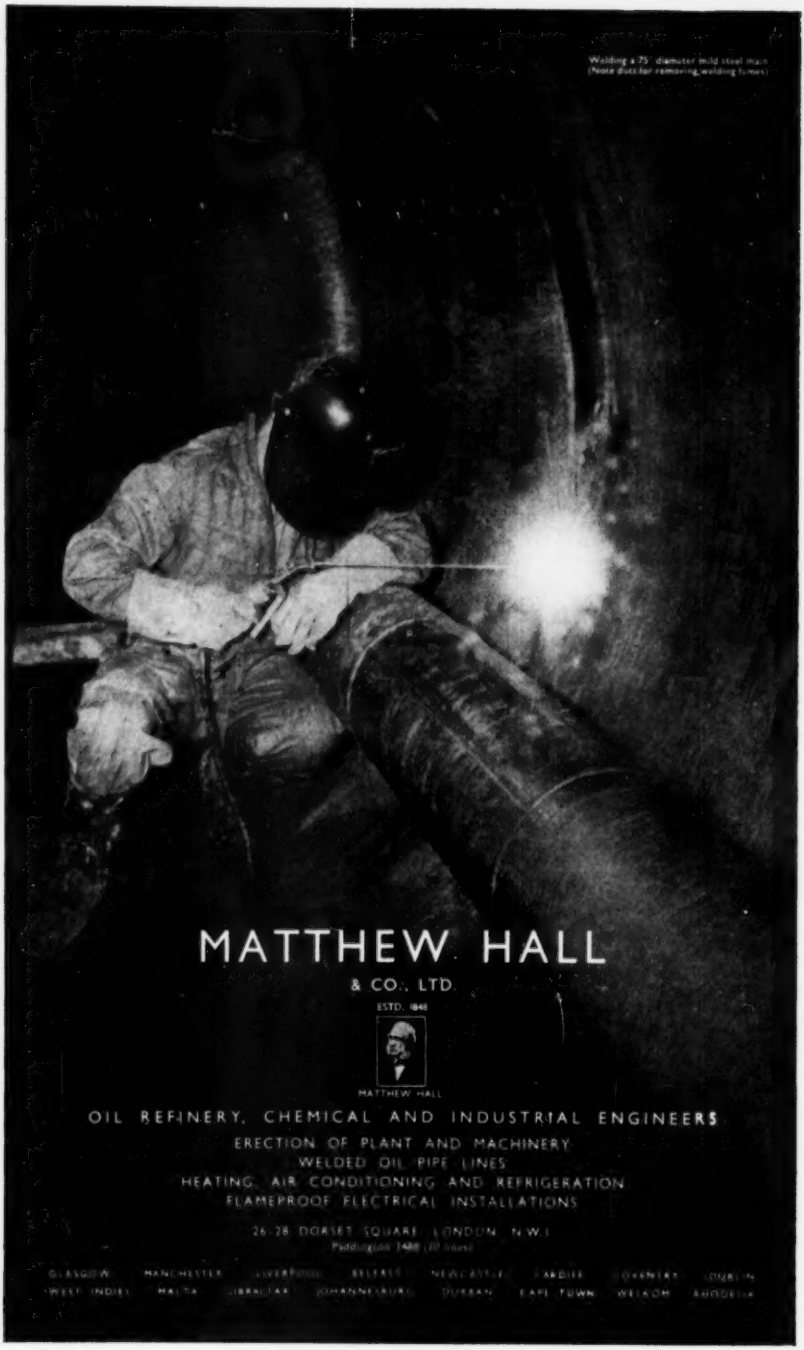
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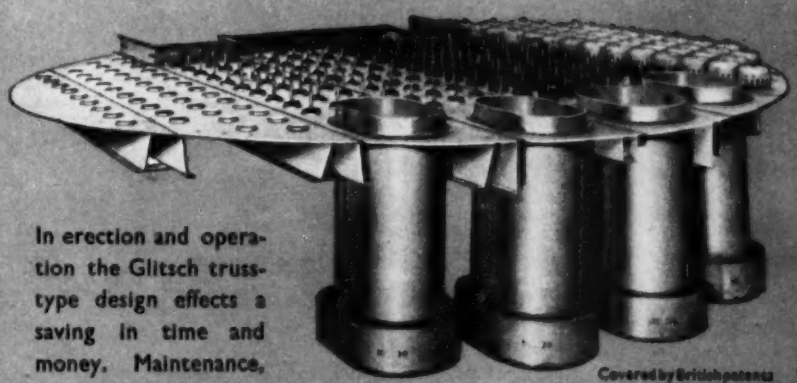

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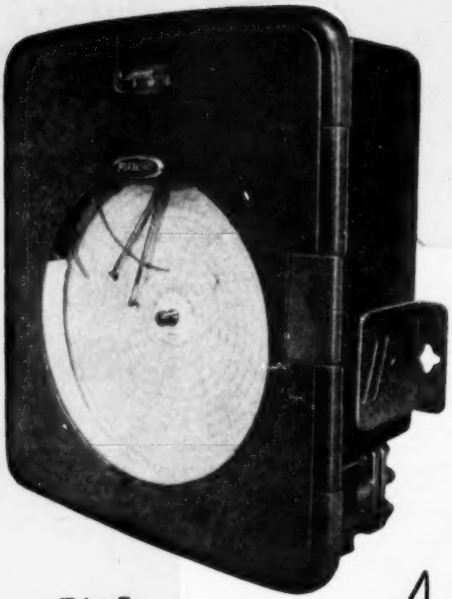

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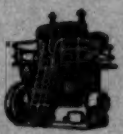

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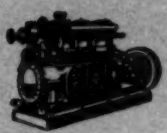

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